

STATEMENT

I, Naoshi KITAMURA—of ARK Mori Building, 13F, 12-32, Akasaka 1-chome, Minato-ku, Tokyo 107-6013 Japan—hereby declare that I am conversant in both Japanese and English and that I believe the following is a true and correct translation of a certified copy of Japanese Patent Application No. 2002-382231.

Date: June 24, 2005

A handwritten signature in cursive script, appearing to read 'N. Kitamura', written over a horizontal line.

Naoshi KITAMURA

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following
application as filed with this Office.

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(Article) Abstract 1 copy

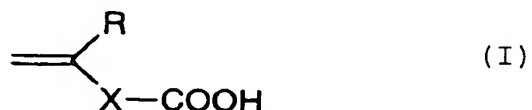
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[Name of Document] Specification

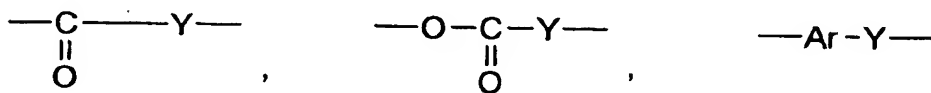
[Title of the Invention] INFRARED PHOTSENSITIVE
LITHOGRAPHIC PRINTING PLATE PRECURSOR

[Scope of Claims for a Patent]

[Claim 1] An infrared photosensitive lithographic printing plate precursor comprising a support having thereon two layers each containing a resin insoluble in water and soluble in an aqueous alkaline solution, wherein an upper layer of the two layers contains a copolymer including a monomer unit represented by formula (I) shown below,



wherein R represents a hydrogen atom or a alkyl group, and X represents an arylene group, which may have a substituent, or any one of the structures shown below;



wherein Ar represents an arylene group which may have a substituent, and Y represents a divalent connecting group.

[Detailed Description of the Invention]

[Technical Field of the Invention]

The present invention relates to a photosensitive lithographic printing plate precursor. Particularly, it

relates to an infrared photosensitive lithographic printing plate precursor for a so-called direct plate-making, which is capable of producing a printing plate directly from digital data of a computer or the like. More particularly, it relates an infrared photosensitive lithographic printing plate precursor which exhibits a broad development latitude and is excellent in scratch resistance.

[Background Art]

The progress of lasers in recent years has been remarkable and high output and compact devices of solid laser or semiconductor laser having a light emission region in the range of from near infrared to infrared become easily available. The infrared photosensitive lithographic printing plate precursor for direct plate-making directly from digital data of a computer or the like, which is used such an infrared laser as a light source, is useful because it can be handled in a bright room and is very preferable in the plate-making operation.

As the infrared photosensitive lithographic printing plate precursor for direct plate-making, a negative-working lithographic printing plate precursor having an infrared absorbing agent, a compound capable of generating an acid upon application of heat (an acid-forming agent), a crosslink agent capable of performing cross-linking

reaction upon heat, and a binder polymer. However, in such a negative-working lithographic printing plate precursor, it is necessary to heat the printing plate precursor for cross-linking reaction after exposure. As a result, there is a problem in complication operation due to increasing the number of steps and high energy consumption due to the heating.

For such problems, as the infrared photosensitive lithographic printing plate precursor, which does not require the heating after exposure, a positive-working infrared photosensitive lithographic printing plate precursor having a recording layer comprising a binder resin soluble in an aqueous alkaline solution and an infrared absorbing agent (an infrared absorbing dye or the like), which absorbs light to generate heat, is proposed. In such a positive-working photosensitive lithographic printing plate precursor, the infrared absorbing dye or the like in the unexposed area (image area) serves as a dissolution inhibiting agent, which interacts with the binder resin to substantially decrease a solubility of the binder resin. On the other hand, in the exposed area (non-image area), the interaction between the infrared absorbing dye or the like and the binder resin is weakened upon the heat generated by the exposure so that the binder resin becomes soluble in an alkali developing solution.

Development is conducted using such difference of the solubility between the exposed area and the unexposed area, whereby a lithographic printing plate is prepared.

However, in such a positive-working heat-sensitive lithographic printing plate precursor, there is a problem in that the difference between the dissolution resistance of the unexposed area (image area) to the developing solution and the solubility of the exposed area (non-image area) in the developing solution in various using conditions is yet insufficient, and an excessive development (phenomenon of reduction of film thickness, in which the image layer becomes thin due to the dissolution of the image area) or an inferior development (phenomenon of the occurrence of residual film, in which the non-image area is not completely dissolved and remains) is apt to occur by the fluctuation of the using conditions. Further, since strength of the image-recording layer is low, there is a problem in that the surface state readily fluctuates, for example, fine scratches are generated even by touching with the surface at the handling, and such slight fluctuation of the surface state, for example, the fine scratches, causes increase of the solubility in the vicinity thereof, as a result, the scratch trace is left in the unexposed area (image area) after development,

resulting in the occurrence of deterioration of printing durability or inking failure.

Those problems are derived from essential difference in plate-making mechanism between an infrared photosensitive lithographic printing plate precursor and a photosensitive lithographic printing plate precursor for plate-making through UV exposure. Specifically, in the photosensitive lithographic printing plate precursor for plate-making through UV exposure, a binder resin soluble in an aqueous alkaline solution and an onium salt or quinonediazide compound are essential components. The onium salt or quinonediazide compound performs two functions. One is a function as dissolution inhibiting agent upon interaction with the binder resin in the unexposed area (image area), and the other is a function as dissolution accelerating agent by generating an acid upon decomposition with light in the exposed area (non-image area).

On the other hand, the infrared absorbing dye or the like contained in the infrared photosensitive lithographic printing plate precursor acts only as the dissolution inhibiting agent in the unexposed area (image area), and does not accelerate the dissolution in the exposed area (non-image area). Therefore, in order to make difference in solubility between the unexposed area and the exposed

area in the infrared photosensitive lithographic printing plate precursor, it cannot be helped to use as the binder resin a resin essentially having high solubility in an alkali developing solution. Thus, the infrared photosensitive lithographic printing plate precursor bears problems in that the reduction of film thickness occurs, in that the scratch resistance is deteriorated and that the states before development are unstable. On the contrary, when the solubility of the binder resin in the alkali developing solution is decreased in order to strengthen the unexposed area, decrease in sensitivity is caused. Accordingly, a range of development condition (development latitude) for forming an image by distinguishing of the difference in solubility is narrowly restricted.

Therefore, various investigations have been made to develop a dissolution inhibiting agent having selectivity, which loses the dissolution inhibiting function in the exposed area but maintains the dissolution inhibiting function in the unexposed area. For instance, a technique of adding a light-heat converting agent and a substance that is thermally decomposable and can substantially decrease solubility of the alkali-soluble resin before it is thermally decomposed to a recording layer of positive-working lithographic printing plate precursor for infrared

laser is described, for example, in Patent Document 1 (JP-A-7-285275). According to the technique, the dissolution of the recording layer is inhibited and the scratch resistance is improved and on the other hand, in the exposed area the substance thermally decomposable is decomposed by heat generated by the light-heat converting agent to lose the dissolution inhibiting function to the alkali-soluble resin, thereby being capable of increasing the sensitivity.

[Patent Document 1]

JP-A-7-285275

[Disclosure of the Invention]

[Problems that the Invention is to Solve]

However, the development latitude and the scratch resistance in the above-described technique have been still insufficient and the improvement has been demanded.

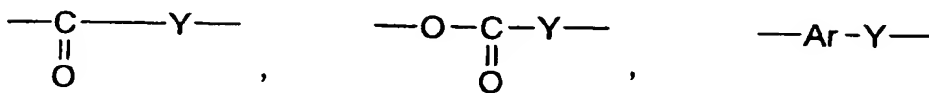
Accordingly, an object of the invention is to overcome the problems in the prior art on the photosensitive lithographic printing plate precursor for an infrared laser and for a so-called direct plate-making, which is capable of producing a printing plate directly from digital data of a computer or the like. More specifically, an object of the invention is to provide a infrared photosensitive lithographic printing plate

precursor, which exhibits a broad development latitude and is excellent in scratch resistance.

As a result of the intensive investigations, it has been found that the above-described objects can be achieved by an infrared photosensitive lithographic printing plate precursor comprising a support having thereon two layers each containing a resin insoluble in water and soluble in an aqueous alkaline solution, wherein an upper layer of the two layers contains a copolymer including a monomer unit represented by formula (I) shown below,



wherein R represents a hydrogen atom or a alkyl group, and X represents an arylene group, which may have a substituent, or any one of the structures shown below,



wherein Ar represents an arylene group which may have a substituent, and Y represents a divalent connecting group.

The invention is based on the finding resulting from the intensive investigations that discrimination on development, that is, distinction between the image area and the non-image area, is considerably improved by

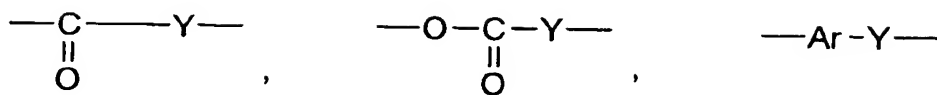
forming image-forming layers of a two-layer structure each containing a resin insoluble in water and soluble in an aqueous alkaline solution and being incorporated a specific resin soluble in an aqueous alkaline solution into the upper layer. As a result of the increase of the discrimination, significant improvements in the development altitude and scratch resistance can be achieved.

[Mode for Carrying Out the Invention]

An infrared photosensitive lithographic printing plate precursor of the invention includes a support having thereon two layers each containing a resin insoluble in water and soluble in an aqueous alkaline solution (hereinafter also referred to as an alkali-soluble resin sometimes), in which an upper layer (layer far from the support) of the two layers contains a copolymer including a monomer unit represented by formula (I) shown below.



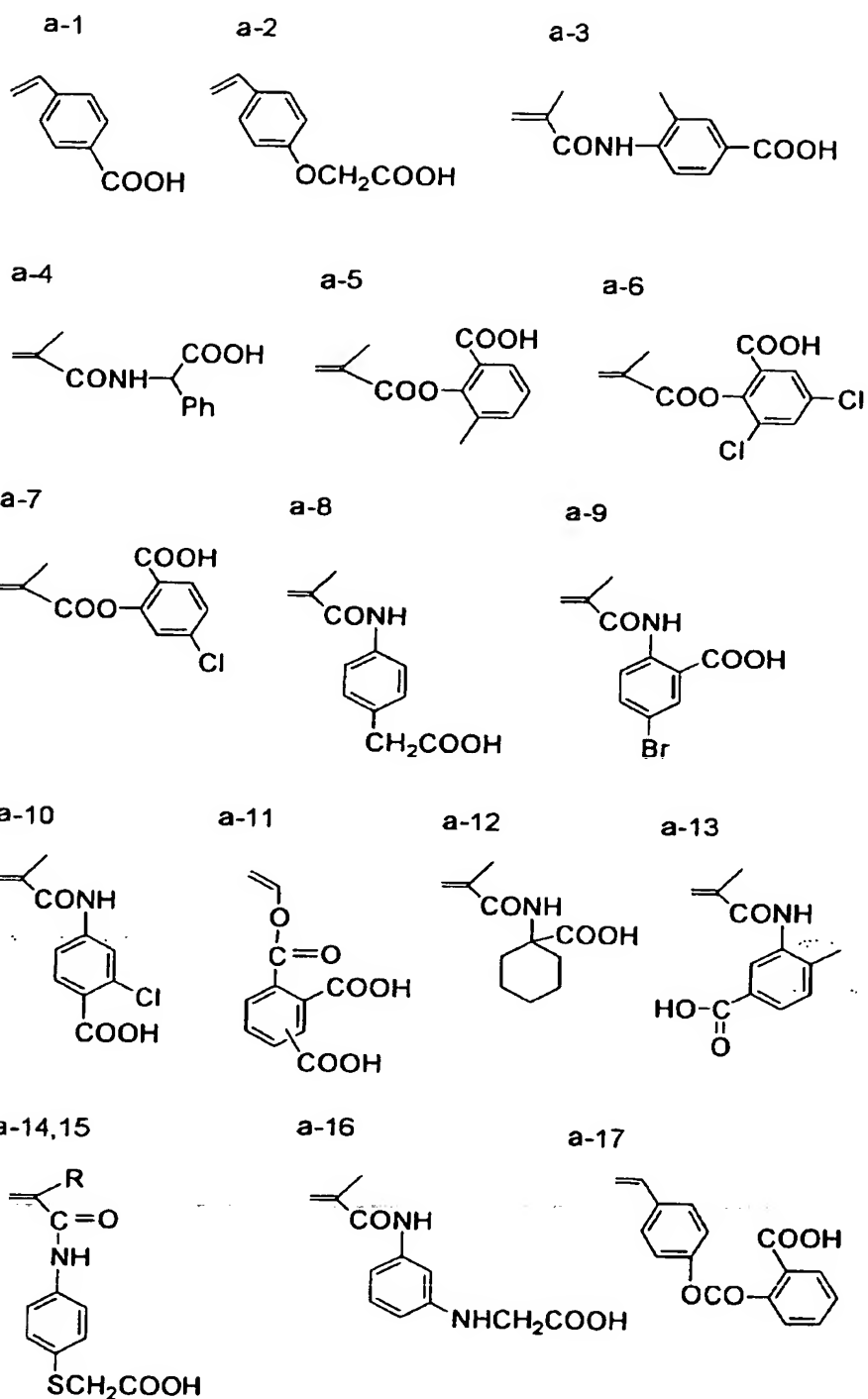
In formula (I), R represents a hydrogen atom or an alkyl group, preferably an alkyl group having 1 to 4 carbon atoms. X represents an arylene group, which may have a substituent, or any one of the structures shown below,



wherein Ar represents an arylene group which may have a substituent, and Y represents a divalent connecting group.

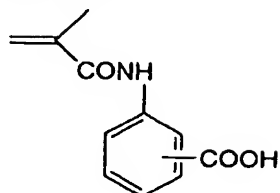
The divalent connecting group represented by Y includes an alkylene group, an arylene group, an imido group and an alkoxy group, each of which may have a substituent. Examples of the substituent include an alkyl group, a hydroxy group, an alkoxy group, a halogen atom, a phenyl group, a dimethylamino group, an ethylene oxide group, a vinyl group and an o-carboxybenzoyloxy group.

Specific examples of the monomer represented by formula (I) are set forth below, but the invention should not be construed as being limited thereto.



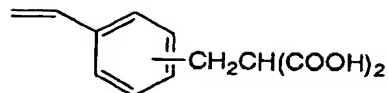
a-14: R= -H, a-15: R= -CH₃

a-18,19,20

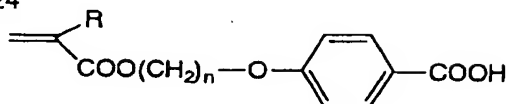


a-18: o-
a-19: m-
a-20: p-

a-21

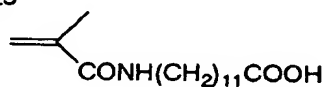


a-22,23,24

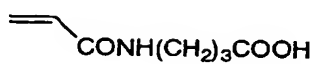


a-22: R=CH3, n=4
a-23: R=CH3, n=6
a-24: R=H, n=6

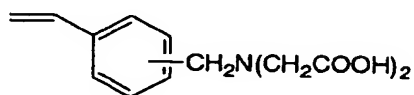
a-25



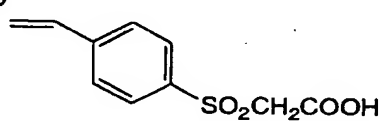
a-26



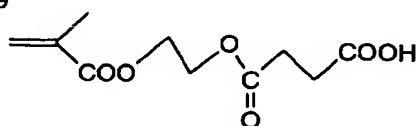
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a-28



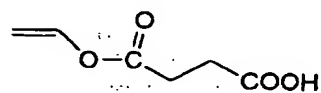
a-29



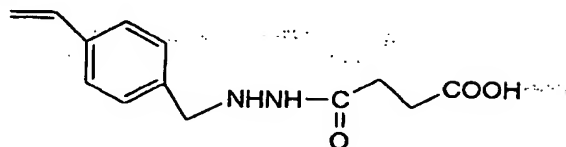
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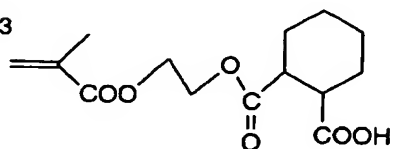
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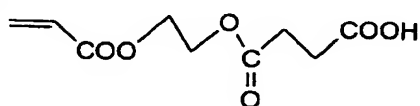
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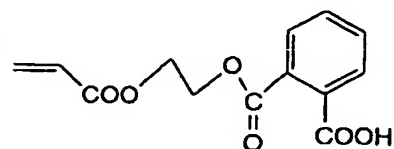
a-33



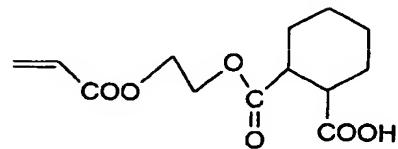
a-34



a-35



a-36



The content of monomer represented by formula (I) is preferably from 1 to 90% by mole, more preferably from 2 to 50% by mole, and still more preferably from 5 to 35% by mole. In the above-described range, the favorable developing property and ratio of residual film in the unexposed area are obtained.

The copolymerizable monomer component, which is copolymerized with the monomer represented by formula (I) to form copolymer, includes a (meth)acrylate, a (meth)acrylamide derivative and a styrene derivative. The copolymerizable monomer component may be composed of one kind, or appropriate two kinds or three kinds or more of monomers selected from the (meth)acrylate (meth)acrylamide derivative and styrene derivative. Specifically, the copolymerizable monomer component may be four kinds of monomers in total composed of two kinds of monomers selected from the (meth)acrylate and two kinds of monomers selected from the styrene derivative.

In the specification, acryl and methacryl are collectively referred to as "(meth)acryl". The terminology "include a (meth)acrylate as a copolymer component" as used herein means that at least any one of acrylate and methacrylate is included. The same is also applied to a (meth)acrylamide derivative.

The (meth)acrylate as the copolymerizable monomer component described above includes substituted or unsubstituted alkyl esters and aryl esters. The alkyl group includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-hexyl, n-heptyl, n-octyl and 2-ethylhexyl. The aryl group includes, for example, phenyl, 1-naphthyl, 2-naphthyl and benzyl. The alkyl group or aryl group may have a substituent. Examples of the substituent include a hydroxy group, an alkoxy group, a halogen atom, a phenyl group, a dimethylamino group, an ethylene oxide group, a vinyl group and an o-carboxybenzoyloxy group.

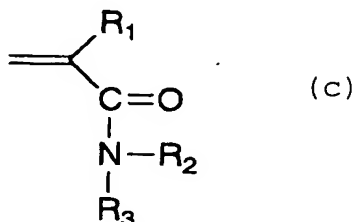
The (meth)acrylate for use in the invention preferably includes methyl acrylate, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-butyl methacrylate.

The (meth)acrylates may be used individually or in combination of two or more thereof in the invention.

The content of the (meth)acrylate is preferably from 0 to 95% by mole, more preferably from 5 to 90% by mole, and still more preferably from 10 to 80% by mole in the copolymer.

The (meth)acrylamide derivative constituting the copolymerizable monomer component according to the invention is not particularly limited as long as it is a

derivative of (meth)acrylamide, but preferably a (meth)acrylamide derivative represented by the following formula (c):



In formula (c), R₁ represents a hydrogen atom or an alkyl group. R₂ and R₃ each independently represent a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms or an aryl group having from 6 to 10 carbon atoms, provided that both R₂ and R₃ are not hydrogen atoms at the same time.

R₁ in formula (c) represents a hydrogen atom or an alkyl group and preferably a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms.

The alkyl group having from 1 to 10 carbon atoms for R₂ or R₃ includes, for example, methyl, ethyl, n-propyl, n-butyl, isobutyl, tert-butyl, n-hexyl, n-heptyl, n-octyl and 2-ethylhexyl. The aryl group having from 6 to 10 carbon atoms for R₂ or R₃ includes, for example, phenyl, 1-naphthyl or 2-naphthyl. The alkyl group or aryl group may have a substituent. Examples of the substituent include a hydroxy group, an alkoxy group, a halogen atom, a phenyl group, a dimethylamino group, an ethylene oxide group, a

vinyl group and an o-carboxybenzoyloxy group. Both R_2 and R_3 are not hydrogen atoms at the same time.

Specific examples of the (meth)acrylamide derivative are set forth below, but the invention should not be construed as being limited thereto.

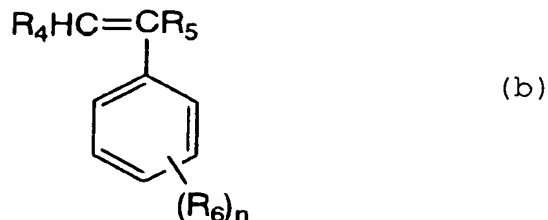
- (c-1) N-tert-Butylacrylamide
- (c-2) N-(n-Butoxymethyl)acrylamide
- (c-3) N-tert-Butylmethacrylamide
- (c-4) N-(1,1-Dimethyl-3-oxobutyl)acrylamide
- (c-5) N,N-Dimethylmethacrylamide
- (c-6) N,N-Dimethylacrylamide
- (c-7) N-Isopropylacrylamide
- (c-8) N-Methylmethacrylamide
- (c-9) N-Phenylmethacrylamide
- (c-10) N-[3-(Dimethylamino)propyl]acrylamide

The (meth)acrylamide derivatives may be used individually or in combination of two or more thereof in the copolymerizable monomer component.

The content of the (meth)acrylamide derivative is preferably from 0 to 95% by mole, more preferably from 5 to 90% by mole, and still more preferably from 20 to 80% by mole in the copolymer.

The styrene derivative constituting the copolymerizable monomer component according to the invention is not particularly limited as long as it is a

derivative of styrene, but preferably a styrene derivative represented by the following formula (b):



In formula (b), R_4 , R_5 and R_6 each independently represent a hydrogen atom or a substituent. n represents an integer of from 1 to 5. The substituent for R_4 , R_5 or R_6 is not particularly limited and includes an alkyl group, an aryl group, a hydroxy group, a carboxy group and a halogen atom.

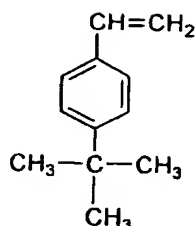
Specific examples of the styrene derivative are set forth below, but the invention should not be construed as being limited thereto.

- (b-1) 4-Bromostyrene
- (b-2) β -Bromostyrene
- (b-3) 4-Chloro- α -methylstyrene
- (b-4) 3-Chlorostyrene
- (b-5) 4-Chlorostyrene
- (b-6) 2,6-Dichlorostyrene
- (b-7) 2-Fluorostyrene
- (b-8) 3-Fluorostyrene
- (b-9) 4-Fluorostyrene
- (b-10) Methylstyrene

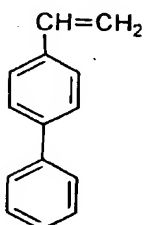
(b-11) Vinyltoluene

(b-12) trans- β -Methylstyrene

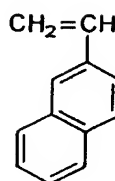
b-13



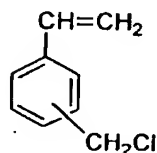
b-14



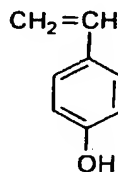
b-15



b-16



b-17



Besides the above examples, the styrene derivative includes, for example, styrene, vinyl benzoate, methyl vinyl benzoate, hydroxymethylstyrene, sodium p-styrenesulfonate, potassium p-styrenesulfinate, p-aminomethylstyrene and 1,4-divinylbenzene. The styrene derivatives may be used individually or in combination of two or more thereof in the copolymerizable monomer component.

The content of the styrene derivative is preferably from 0 to 95% by mole, more preferably from 5 to 90% by mole, and still more preferably from 20 to 80% by mole in the copolymer.

The copolymer obtained from the monomer of formula (I) and the copolymerizable monomer component itself brings about preferable physical properties, for example, preferable development latitude. By further copolymerization of a third copolymerizable monomer component, other various physical properties can be improved or modified. Such other various physical properties include, for example, chemical resistance, printing durability, sensitivity and developing property. Examples of the third copolymerizable monomer component include acrylonitrile, maleimide, vinyl acetate and N-vinylpyrrolidone.

The weight average molecular weight of the copolymer for use in the invention is preferably from 5,000 to 200,000, more preferably from 10,000 to 120,000, and particularly preferably from 20,000 to 80,000. In the above range of the weight average molecular weight, the sufficient film-forming property and favorable development property are obtained.

As a copolymerization method for forming the copolymer, for example, a conventionally known graft copolymerization method, block copolymerization method or random copolymerization method can be used.

The content of the copolymer including the monomer unit represented by formula (I) is preferably from 1 to

40% by weight, and more preferably from 2 to 30% by weight based on the total solid content of the upper layer. The content more than 40% by weight is not preferred because the printing durability in burning treatment is lowered.

The upper layer according to the invention contains as the essential component the copolymer including the monomer unit represented by formula (I) and may further contain other alkali-soluble resin. The alkali-soluble resin included in the upper layer is described below. The alkali-soluble resin can also be used as an alkali-soluble resin for a layer (lower layer) close to the support. It is possible to incorporate the copolymer including the monomer unit represented by formula (I) into the lower layer as the alkali-soluble resin. In such a case, however, it is preferred that the addition ratio of the copolymer in the lower layer is lower than the addition ratio of the copolymer in the upper layer.

(Alkali-soluble resin)

The alkali-soluble resin includes a homopolymer or copolymer containing an acidic group in the main chain and/or side chain thereof, and a mixture thereof. Accordingly, the layer including the alkali-soluble resin in the invention have a feature of dissolving upon contact with an alkaline developing solution.

The alkali-soluble resin is not particularly limited and conventionally known alkali-soluble resin can be used. A resin having any one functional group of (1) a phenolic hydroxy group, (2) a sulfonamido group and (3) an active imido group is preferred.

Examples of the resin include those described below, but the invention should not be construed as being limited thereto.

(1) Examples of the polymer compound having a phenolic hydroxy group include novolak resins, for example, phenol formaldehyde resin, m-cresol formaldehyde resin, p-cresol formaldehyde resin, m-/p-mixed cresol formaldehyde resin and phenol/cresol (the cresol may be any one of m-cresol, p-cresol and m-/p-mixed cresol) mixed formaldehyde resin, and pyrogallol acetone resins. A polymer compound having a phenolic hydroxy group in its side chain is also exemplified as the polymer compound having a phenolic hydroxy group. Examples of the polymer compound having a phenolic hydroxy group in its side chain include polymer compounds obtained by homopolymerization of a polymerizable monomer of a low molecular compound having one or more phenolic hydroxy groups and one or more polymerizable unsaturated bonds, or copolymerization of such a monomer with other polymerizable monomer.

Examples of the polymerizable monomer having a phenolic hydroxy group include an acrylamide, a methacrylamide, an acrylate and a methacrylate each having a phenolic hydroxy group and a hydroxystyrene. Specifically, N-(2-hydroxyphenyl)acrylamide, N-(3-hydroxyphenyl)acrylamide, N-(4-hydroxyphenyl)acrylamide, N-(2-hydroxyphenyl)methacrylamide, N-(3-hydroxyphenyl)methacrylamide, N-(4-hydroxyphenyl)methacrylamide, o-hydroxyphenyl acrylate, m-hydroxyphenyl acrylate, p-hydroxyphenyl acrylate, o-hydroxyphenyl methacrylate, m-hydroxyphenyl methacrylate, p-hydroxyphenyl methacrylate, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, 2-(2-hydroxyphenyl)ethyl acrylate, 2-(3-hydroxyphenyl)ethyl acrylate, 2-(4-hydroxyphenyl)ethyl acrylate, 2-(2-hydroxyphenyl)ethyl methacrylate, 2-(3-hydroxyphenyl)ethyl methacrylate and 2-(4-hydroxyphenyl)ethyl methacrylate are preferably used. The resins having a phenolic hydroxy group may be used in combination of two or more thereof. In addition, a condensation polymerization product of a phenol containing as a substituent an alkyl group having from 3 to 8 carbon atoms with formaldehyde, for example, tert-butylphenol formaldehyde resin or octylphenol formaldehyde resin described in U.S. Patent 4,123,279 may be used together.

(2) Examples of the alkali-soluble polymer compound having a sulfonamido group include polymer compounds obtained by homopolymerization of a polymerizable monomer having a sulfonamido group, or copolymerization of such a monomer with other polymerizable monomer. Examples of the polymerizable monomer having a sulfonamido group include a polymerizable monomer of a low molecular compound having one or more sulfonamido groups having at least one hydrogen atom bonded on the nitrogen atom thereof, which is represented by $\text{-NH-SO}_2\text{-}$, and one or more polymerizable unsaturated bonds. Among them, low molecular compounds having both an acryloyl group, an allyl group or a vinyloxy group and an unsubstituted or mono-substituted aminosulfonyl group or a substituted sulfonylimino group are preferred.

(3) The alkali-soluble polymer compound having an active imido group preferably has the active imido group in its molecule. Examples of the polymer compound include polymer compounds obtained by homopolymerization of a polymerizable monomer of a low molecular compound having one or more active imido groups and one or more polymerizable unsaturated bonds in its molecule, or copolymerizing such a monomer with other polymerizable monomer.

Specific examples of such a monomer, which can be favorably used, include N-(p-toluenesulfonyl)methacrylamide and N-(p-toluenesulfonyl)acrylamide.

Further, as the alkali-soluble resin, a polymer in which at least two monomer of a polymerizable monomer having a phenolic hydroxy group, a polymerizable monomer having a sulfonamido group and a polymerizable monomer an active imido group are polymerized, or a polymer in which the at least two monomer are copolymerized with another polymerizable monomer is preferred. When the polymerizable monomer having the phenolic hydroxy group is copolymerized with a polymerizable monomer having a sulfonamido group and/or a polymerizable monomer an active imido group, a weight ratio of the former component to the latter component is preferably from 50:50 to 5:95, more preferably from 40:60 to 10:90.

In a photosensitive lithographic printing plate precursor of the invention, when the alkali-soluble resin is a copolymer of a polymerizable monomer having a phenolic hydroxy group, a polymerizable monomer having a sulfonamido group, or a polymerizable monomer an active imido group and another polymerizable monomer, the resin include a monomer imparting the alkali-soluble property in an amount of preferably 10% by mole or more, more

preferably 20% by mole or more. When the amount is not more than 10% by mole, the alkali-soluble property is apt to be insufficient and the effect of increasing the development latitude is apt to be lowered.

Examples of the monomer copolymerized with the polymerizable monomer having a phenolic hydroxy group, the polymerizable monomer having a sulfonamido group or the polymerizable monomer having an active imido group include compounds set forth in the following (n1) to (n12), however, the invention should not be construed as being limited thereto.

As a copolymerization method for forming the copolymer, for example, a conventionally known graft copolymerization method, block copolymerization method or random copolymerization method can be used.

- (m1) Acrylates and methacrylates, each having an aliphatic hydroxy group, for example, 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate.
- (m2) Alkyl acrylates, for example, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, benzyl acrylate, 2-chloroethyl acrylate or glycidyl acrylate.
- (m3) Alkyl methacrylates, for example, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate or glycidyl methacrylate.
- (m4) Acrylamides and methacrylamides, for example, acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide,

- N-phenylacrylamide, N-nitrophenylacrylamide or N-ethyl-N-phenylacrylamide.
- (m5) Vinyl ethers, for example, ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether or phenyl vinyl ether.
 - (m6) Vinyl esters, for example, vinyl acetate, vinyl chloroacetate, vinyl butyrate or vinyl benzoate.
 - (m7) Styrenes, for example, styrene, α -methylstyrene, methylstyrene or chloromethylstyrene.
 - (m8) Vinyl ketones, for example, methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone or phenyl vinyl ketone.
 - (m9) Olefins, for example, ethylene, propylene, isobutylene, butadiene or isoprene.
 - (m10) N-vinylpyrrolidone, acrylonitrile or methacrylonitrile.
 - (m11) Unsaturated imides, for example, maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide or N-(p-chlorobenzoyl)methacrylamide.
 - (m12) Unsaturated carboxylic acids, for example, acrylic acid, methacrylic acid, maleic anhydride or itaconic acid.

In a photosensitive lithographic printing plate precursor of the invention, when the alkali-soluble resin is a homopolymer or copolymer of the polymerizable monomer having a phenolic hydroxy group, the polymerizable monomer having a sulfonamido group or the polymerizable monomer having an active imido group, the polymer has preferably a weight average molecular weight of not less than 2,000 and a number average molecular weight of not less than 500, and more preferably a weight average molecular weight of from 5,000 to 300,000, a number average molecular weight of from 800 to 250,000 and a dispersion degree (weight

average molecular weight/number average molecular weight) of from 1.1 to 10.

When the alkali-soluble polymer is a resin, for example, phenol formaldehyde resin or cresol aldehyde resin, the polymer preferably has a weight average molecular weight of from 500 to 20,000 and a number average molecular weight of from 200 to 10,000.

In a photosensitive lithographic printing plate precursor of the invention, the alkali-soluble resin for use in the upper layer is preferably a resin having a phenolic hydroxy group in view of solubility in the developer and solubility in the coating solvent. The alkali-soluble resin for use in lower layer is preferably the above-described (2) an alkali-soluble polymer having a sulfonamido group or (3) an alkali-soluble polymer having an active imido group in view of solubility in the developer and solubility in the coating solvent.

These alkali-soluble resins each may be used in one kind or in mixture of two or more kinds. The amount of the alkali-soluble resin in the lower layer is preferably, a mixing ratio thereof can be appropriately selected. It is preferred, however, that the content of the alkali-soluble polymer compound having a phenolic hydroxy group is not less than 60% by weight based on the total alkali-soluble polymer compound.

The amount of the alkali-soluble polymer compound added to the upper image-forming layer is from 30 to 99% by weight, preferably from 40 to 95% by weight, more preferably from 50 to 90% by weight in total solid content.

When the amount of the alkali-soluble polymer compound is not more than 30% by weight, the durability of the lower layer is deteriorated. On the other hand, when it is not less than 99% by weight, it is not preferred in both the sensitivity and the durability.

(Infrared absorbing agent)

Into each layer including the alkali-soluble resin according to the invention, an infrared absorbing agent (hereinafter referred as to an infrared absorbing dye sometimes) can be incorporated for the purpose of promoting the efficiencies of light absorption and light-heat conversion, thereby increasing the sensitivity.

The infrared absorbing agent is not particularly limited as long as it is a dye capable of absorbing infrared light to generate heat, and various kinds of dyes known as infrared absorbing dyes can be used.

Examples of the infrared absorbing dye, which can be used in the invention, include commercially available dyes and known dyes described in literature, for example, Yuki Gosei Kagaku Kyokai ed., Senryo Binran (Handbook of Dyes) (1970). Specific examples thereof include dyes, for

example, azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinonimine dyes, methine dyes and cyanine dyes. Of these dyes, those absorbing infrared or near infrared light are particularly preferred in the invention, because they are suitable for use with a laser emitting infrared or near infrared light.

Examples of the dye absorbing infrared or near infrared light include cyanine dyes described in JP-A-58-125246, JP-A-59-84356, JP-A-60-78787 and U.S. Patent 4,973,572, methine dyes described in JP-A-58-173696, JP-A-58-181690 and JP-A-58-194595, naphthoquinone dyes described in JP-A-58-112793, JP-A-58-224793, JP-A-59-48187, JP-A-59-73996, JP-A-60-52940 and JP-A-60-63744, squarylium dyes described in JP-A-58-112792 and cyanine dyes described in British Patent 434,875.

Other examples of the dye preferably used include near infrared absorbing sensitizers described in U.S. Patent 5,156,938, substituted arylbenzo(thio)pyrylium salts described in U.S. Patent 3,881,924, trimethinethiapyrylium salts described in JP-A-57-142645, pyrylium compounds described in JP-A-58-181051, JP-A-58-220143, JP-A-59-41363, JP-A-59-84248, JP-A-59-84249, JP-A-59-146063 and JP-A-59-146061, cyanine dyes described in JP-A-59-216146, pentamethinethiopyrylium salts described

in U.S. Patent 4,283,475, pyrylium compounds described in JP-B-5-13514 and JP-B-5-19702, near infrared absorbing dyes represented by formulae (I) and (II) in U.S. Patent 4,765,993, and commercially available products, for example, Epolight III-178, Epolight III-130 or Epolight III-125 (manufactured by Epolin Inc.).

Another examples of the dye include an near-infrared absorbing dye disclosed in the specification of U.S. Patent 4,756,993 as formula (I) or (II).

The amount of the infrared absorbing dye added to each layer in a photosensitive lithographic printing plate precursor of the invention is ordinarily from 0.01 to 50% by weight, preferably from 0.1 to 30% by weight, and particularly preferably from 1.0 to 30% by weight based on the total solid content of the each layer. When the amount is not more than 0.01% by weight, the sensitivity is apt to be lowered. When it is not less than 50% by weight, the uniformity of each layer is damaged and the durability of each layer is apt to be lowered.

(Dissolution inhibiting compound)

The photosensitive lithographic printing plate precursor of the invention can contain a variety of dissolution inhibiting compounds (inhibitors) in the upper layer and/or the lower layer for the purpose of increasing

the dissolution inhibition (inhibition) of the image area thereof.

The inhibitor is not particularly limited and includes, for example, a quaternary ammonium salt and a polyethylene glycol compound.

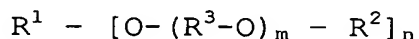
The quaternary ammonium salt used is not particularly restricted and includes tetraalkylammonium salts, trialkylarylammonium salts, dialkyldiarylammonium salts, alkyltriarylammonium salts, tetraarylammonium salts, cyclic ammonium salts and bicyclic ammonium salts.

Specific examples of the quaternary ammonium salt include tetrabutylammonium bromide, tetrapentylammonium bromide, tetrahexylammonium bromide, tetraoctylammonium bromide, tetralaurylammonium bromide, tetraphenylammonium bromide, tetranaphthylammonium bromide, tetrabutylammonium chloride, tetrabutylammonium iodide, tetrastearylammonium bromide, lauryltrimethylammonium bromide, stearyltrimethylammonium bromide, behenyltrimethylammonium bromide, lauryltriethylammonium bromide, phenyltrimethylammonium bromide, 3-trifluoromethylphenyltrimethylammonium bromide, benzyltrimethylammonium bromide, dibenzyltrimethylammonium bromide, distearyldimethylammonium bromide, tristearylmethylammonium bromide, benzyltriethylammonium

bromide, hydroxyphenyltrimethylammonium bromide and N-methylpyridinium bromide.

The amount of the quaternary ammonium salt added is preferably from 0.1 to 50% by weight, and more preferably from 1 to 30% by weight based on the total solid content of the upper layer. When the amount is not more than 0.1% by weight, the dissolution inhibiting effect is lowered. The addition in exceeding 50% by weight may be apt to exert a bad influence upon the film-forming property of the binder.

The polyethylene glycol compound used is not particularly restricted and examples thereof include compounds having a structure represented by the following formula:



wherein R^1 represents a polyhydric alcohol residue or a polyhydric phenol residue, R^2 represents a hydrogen atom, an alkyl group having from 1 to 25 carbon atoms, an alkenyl group, an alkynyl group, an alkyloyl group, an aryl group or an aryloyl group, each of which may have a substituent, R^3 represents an alkylene group, which may have a substituent, m represents a number of not less than 10 on the average, and n represents an integer of from 1 to 4.

Examples of the polyethylene glycol compound having the structure represented by the formula described above include polyethylene glycols, polypropylene glycols, polyethylene glycol alkyl ethers, polypropylene glycol alkyl ethers, polyethylene glycol aryl ethers, polypropylene glycol aryl ethers, polyethylene glycol alkyl aryl ethers, polypropylene glycol alkyl aryl ethers, polyethylene glycol glycerol esters, polypropylene glycol glycerol esters, polyethylene glycol sorbitol esters, polypropylene glycol sorbitol esters, polyethylene glycol fatty acid esters, polypropylene glycol fatty acid esters, polyethylene glycolated ethylenediamines, polypropylene glycolated ethylenediamines, polyethylene glycolated diethylenetriamines and polypropylene glycolated diethylenetriamines.

Specific examples thereof include polyethylene glycol 1000, polyethylene glycol 2000, polyethylene glycol 4000, polyethylene glycol 10000, polyethylene glycol 20000, polyethylene glycol 50000, polyethylene glycol 100000, polyethylene glycol 200000, polyethylene glycol 500000, polypropylene glycol 1500, polypropylene glycol 3000, polypropylene glycol 4000, polyethylene glycol methyl ether, polyethylene glycol ethyl ether, polyethylene glycol phenyl ether, polyethylene glycol dimethyl ether, polyethylene glycol diethyl ether, polyethylene glycol

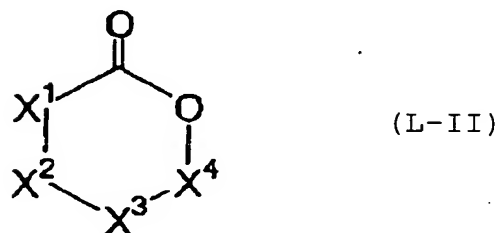
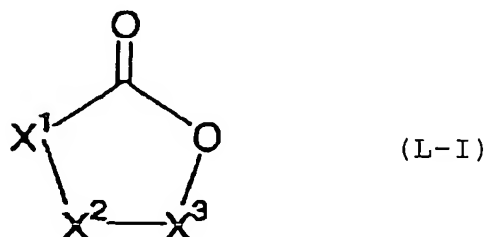
diphenyl ether, polyethylene glycol lauryl ether, polyethylene glycol dilauryl ether, polyethylene glycol nonyl ether, polyethylene glycol cetyl ether, polyethylene glycol stearyl ether, polyethylene glycol distearyl ether, polyethylene glycol behenyl ether, polyethylene glycol dibehenyl ether, polypropylene glycol methyl ether, polypropylene glycol ethyl ether, polypropylene glycol phenyl ether, propylene glycol dimethyl ether, propylene glycol diethyl ether, polypropylene glycol diphenyl ether, polypropylene glycol lauryl ether, polypropylene glycol dilauryl ether, polypropylene glycol nonyl ether, polyethylene glycol acetyl ester, polyethylene glycol diacetyl ester, polyethylene glycol benzoic acid ester, polyethylene glycol lauryl ester, polyethylene glycol dilauryl ester, polyethylene glycol nonylic acid ester, polyethylene glycol cetylic acid ester, polyethylene glycol stearoyl ester, polyethylene glycol distearoyl ester, polyethylene glycol behenic acid ester, polyethylene glycol dibehenic acid ester, polypropylene glycol acetyl ester, polypropylene glycol diacetyl ester, polypropylene glycol benzoic acid ester, propylene glycol dibenzoic acid ester, polypropylene glycol lauric acid ester, polypropylene glycol dilauric acid ester, polypropylene glycol nonylic acid ester, polyethylene glycol glycerol ether, polypropylene glycol glycerol ether,

polyethylene glycol sorbitol ether, polypropylene glycol sorbitol ether, polyethylene glycolated ethylenediamine, polypropylene glycolated ethylenediamine, polyethylene glycolated diethylenetriamine, polypropylene glycolated diethylenetriamine and polyethylene glycolated pentamethylenhexamine.

The amount of the polyethylene glycol compound added is preferably from 0.1 to 50% by weight, and more preferably from 1 to 30% by weight based on the total solid content of each layer. The addition in exceeding 50% by weigh may be apt to accelerate the permeation of the developer due to the polyethylene glycol compound that cannot interact with the binder and to exert a bad influence upon the film-forming property.

When the above-describe inhibition strengthening measure is conducted, the sensitivity may decrease. In such a case, the addition of lactone compound is effective. It is believed that the lactone compound reacts with a developing solution, when the developing solution penetrates into the exposed area, to newly generate a carboxylic acid compound, which contributes to the dissolution of the exposed area, thereby increasing the sensitivity.

The lactone compound used is not particularly restricted and includes compounds represented by the following formulae (L-I) and (L-II):



In formulae (L-I) and (L-II), X^1 , X^2 , X^3 and X^4 each represents an atom or an atomic group constituting a ring, which may be the same or different and may have a substituent, provided that at least one of X^1 , X^2 and X^3 in formula (L-I) and at least one of X^1 , X^2 , X^3 and X^4 in formula (L-II) each have an electron-withdrawing substituent or a substituent substituted with an electron-withdrawing group.

The atom or atomic group constituting a ring represented by X^1 , X^2 , X^3 and X^4 is a non-metallic atom having two single bonds for forming a ring or an atomic group containing the non-metallic atom.

The non-metallic atom or non-metallic atom-containing group is preferably an atom or an atomic group selected from a methylene group, a sulfinyl group, a carbonyl group, a thiocarbonyl group, a sulfonyl group, a sulfur atom, an oxygen atom and a selenium atom, and more preferably an atomic group selected from a methylene group, a carbonyl group or a sulfonyl group.

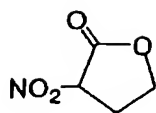
At least one of X^1 , X^2 and X^3 in formula (L-I) and at least one of X^1 , X^2 , X^3 and X^4 in formula (L-II) each have an electron-withdrawing substituent. The term "electron-withdrawing substituent" as used herein means a group, which has a Hammett's substituent constant σ_p of a positive value. With respect to the Hammett's substituent constant, for example, Journal of Medicinal Chemistry, Vol. 16, No. 11, pages 1207 to 1216 (1973) can be referred to. Examples of the electron-withdrawing substituent having the Hammett's substituent constant σ_p of a positive value include a halogen atom (for example, a fluorine atom (σ_p value: 0.06), a chlorine atom (σ_p value: 0.23), a bromine atom (σ_p value: -0.23) or an iodine atom (σ_p value: 0.18)), a trihaloalkyl group (for example, a tribromomethyl group (σ_p value: 0.29), a trichloromethyl group (σ_p value: 0.33) or a trifluoromethyl group (σ_p value: 0.54)), a cyano group (σ_p value: 0.66), a nitro group (σ_p value: 0.78), an aliphatic, aryl or heterocyclic sulfonyl group (for example,

a methanesulfonyl group (σ_p value: 0.72)), an aliphatic, aryl or heterocyclic acyl group (for example, an acetyl group (σ_p value: 0.50) or a benzoyl group (σ_p value: 0.43)), an alkynyl group (for example, an ethynyl group (σ_p value: 0.23)), an aliphatic, aryl or heterocyclic oxycarbonyl group (for example, a methoxycarbonyl group (σ_p value: 0.45) or a phenoxycarbonyl group (σ_p value: 0.44), a carbamoyl group (σ_p value: 0.36), a sulfamoyl group (σ_p value: 0.57), a sulfoxido group, a heterocyclic group, an oxo group and a phosphoryl group.

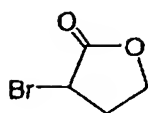
Preferred examples of the electron-withdrawing group include an amido group, an azo group, a nitro group, a nitrile group, an alkoxycarbonyl group having from 1 to 5 carbon atoms, an acyl group having from 1 to 5 carbon atoms, an alkylsulfonyl group having from 1 to 9 carbon atoms, an arylsulfonyl group having from 6 to 9 carbon atoms, an alkylsulfinyl group having from 1 to 9 carbon atoms, an arylsulfinyl group having from 6 to 9 carbon atoms, an arylcarbonyl group having from 6 to 9 carbon atoms, a thiocarbonyl group, a fluorine-containing alkyl group having from 1 to 9 carbon atoms, a fluorine-containing aryl group having from 6 to 9 carbon atoms, a fluorine-containing alkenyl group having from 3 to 9 carbon atoms, an oxo group and a halogen atom.

More preferred examples of the electron-withdrawing group include a nitro group, a fluoroalkyl group having from 1 to 5 carbon atoms, a nitrile group, an alkoxy carbonyl group having from 1 to 5 carbon atoms, an acyl group having from 1 to 5 carbon atoms, an arylsulfonyl group having from 6 to 9 carbon atoms, an arylcarbonyl group having from 6 to 9 carbon atoms, an oxo group and a halogen atom.

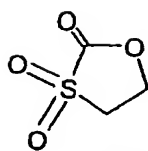
Specific examples of the lactone compound represented by formula (L-I) or (L-II) are set forth below, but the invention should not be construed as being limited thereto.



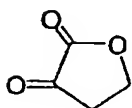
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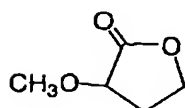
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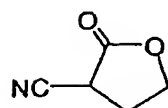
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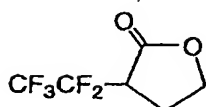
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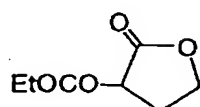
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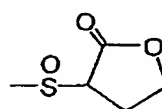
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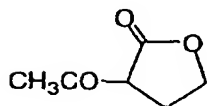
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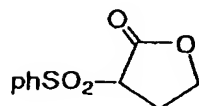
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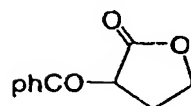
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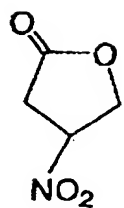
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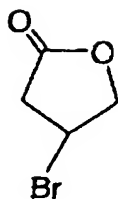
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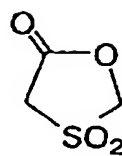
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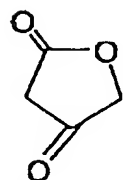
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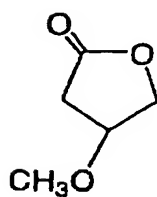
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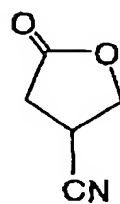
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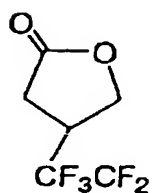
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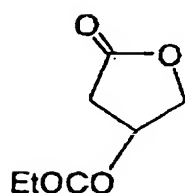
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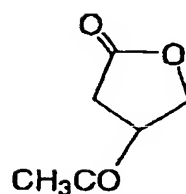
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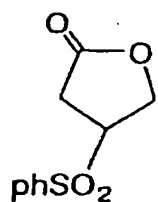
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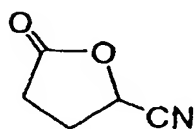
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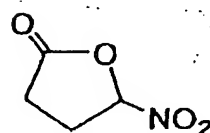
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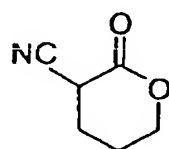
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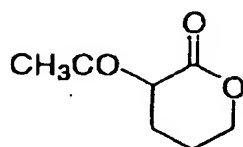
(LI-23)



(LI-24)



(LII-1)



(LII-2)

The amount of the lactone compound represented by formula (L-I) or (L-II) added is from 0.1 to 50% by weight, and preferably from 1 to 30% by weight based on the total solid content of each layer. When the amount is less than 0.1% by weight, the effect is small. When the amount is higher than 50% by weight, the image-forming property may be deteriorated. Since the lactone compound reacts with a developing solution, it is desired to bring the lactone compound into selective contact with the developing solution.

The lactone compounds may be used individually or in combination of two or more thereof. Two or more of the compounds represented by formula (L-I) or two or more of the compounds represented by formula (L-II) may be used in an appropriate proportion as long as the total amount thereof is within the range described above.

It is also preferred that a substance that is thermally decomposable and can substantially decrease solubility of the alkali-soluble resin before being thermally decomposed is incorporated into the photosensitive lithographic printing plate precursor of the invention in view of further enlargement of the difference of solubility between the exposed area and unexposed area.

The substance that is thermally decomposable and can substantially decrease solubility of the alkali-soluble resin before being thermally decomposed is not particularly restricted and examples thereof include various kinds of onium salts and quinonediazide compounds. In view of the thermal decomposing property, the onium salts are preferably used.

Examples of the onium salt include diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts and arsonium salts. Preferred examples of the onium salt for use in the invention include diazonium salts described in S.I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974), T.S. Bal et al., Polymer, 21, 423 (1980) and JP-A-5-158230, ammonium salts described in U.S. Patents 4,069,055, 4,069,056 and U.S. Reissue Patent 27,992; phosphonium salts described in D.C. Necker et al., Macromolecules, 17, 2468 (1984), C.S. Wen et al., Tech. Proc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988) and U.S. Patents 4,069,055 and 4,069,056, iodonium salts described in J.V. Crivello et al., Macromolecules, 10 (6), 1307 (1977), Chem. & Eng. News, p. 31, Nov. 28 (1988), European Patent 104,143, U.S. Patents 339,049 and 410,201, JP-A-2-150848 and JP-A-2-296514, sulfonium salts described in J.V. Crivello et al., Polymer J., 17, 73 (1985), J.V. Crivello

et al., J. Org. Chem., 43, 3055 (1978), W.R. Watt et al., J. Polymer Sci., Polymer Chem. Ed., 22, 1789 (1984), J.V. Crivello et al., Polymer Bull., 14, 279 (1985), J.V. Crivello et al., Macromolecules, 14 (5), 1141 (1981), J.V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 2877 (1979), European Patents 370,693, 3,902,114, 233,567, 297,443 and 297,442, U.S. Patents 4,933,377, 161,811, 410,201, 339,049, 4,760,013, 4,734,444 and 2,833,827 and German Patents 2,904,626, 3,604,580 and 3,604,581, selenonium salts described in J.V. Crivello et al., Macromolecules, 10 (6), 1307 (1977) and J.V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979), and arsonium salts described in C.S. Wen et al., Tech. Proc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988).

In a photosensitive lithographic printing plate precursor of the invention, diazonium salts are particularly preferred. Particularly preferred examples of the diazonium salt include those described in JP-A-5-158230.

Examples of the counter ion of the onium salt include anions formed from tetrafluoroboric acid, hexafluorophosphoric acid, triisopropylphenylsulfonic acid, 5-nitro-o-toluenesulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonic acid, 2,4,6-trimethylbenzenesulfonic acid, 2-nitrobenzenesulfonic acid,

3-chlorobenzenesulfonic acid, 3-bromobenzenesulfonic acid, 2-fluorocaprylnaphthalenesulfonic acid, dodecylbenzenesulfonic acid, 1-naphthol-5-sulfonic acid, 2-methoxy-4-hydroxy-5-benzoylbenzenesulfonic acid and p-toluenesulfonic acid. Among these compounds, hexafluorophosphate and an alkylaromatic sulfonate, for example, triisopropylnaphthalenesulfonate or 2,5-dimethylbenzenesulfonate are preferred. The amount of the above-described compound added is preferably from 0.1 to 50% by weight, more preferably from 0.1 to 30% by weight, and particularly preferably from 0.3 to 30% by weight.

Preferred examples of the quinonediazide compound include o-quinonediazide compounds. The o-quinonediazide compound for use in the invention is a compound having at least one o-quinonediazido group, which increases the alkali solubility upon thermal decomposition, and compounds having various structures can be used. Specifically, o-quinonediazide assists dissolution of the image-forming layer by its two effects, namely, the o-quinonediazide loses the capability of inhibiting the dissolution of the alkali-soluble resin upon thermal decomposition and the o-quinonediazide itself changes into an alkali-soluble substance. Examples of the o-quinonediazide compound, which can be used in the invention, include compounds described in J. Kosar, Light-

Sensitive Systems, pages 339 to 352, John Wiley & Sons, Inc. In particular, sulfonic acid esters or sulfonic acid amides of o-quinonediazide, obtained by reacting with various aromatic polyhydroxy compounds or aromatic amino compounds, are preferred. Also, ester of benzoquinone-(1,2)-diazidosulfonic chloride or naphthoquinone-(1,2)-diazido-5-sulfonic chloride with a pyrogallol-acetone resin described in JP-B-43-28403, and ester of benzoquinone-(1,2)-diazidosulfonic chloride or naphthoquinone-(1,2)-diazido-5-sulfonic chloride with a phenol formaldehyde resin described in U.S. Patents 3,046,120 and 3,188,210 are preferably used.

Furthermore, ester of naphthoquinone-(1,2)-diazido-4-sulfonic chloride with a phenol formaldehyde resin or cresol formaldehyde resin, and ester of naphthoquinone-(1,2)-diazido-4-sulfonic chloride with a pyrogallol-acetone resin are also preferably used. Other useful o-quinonediazide compounds are described in a large number of patents, for example, JP-A-47-5303, JP-A-48-63802, JP-A-48-63803, JP-A-48-96575, JP-A-49-38701, JP-A-48-13354, JP-B-41-11222, JP-B-45-9610, JP-B-49-17481, U.S. Patents 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495 and 3,785,825, British Patents 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932 and German Patent 854,890. The amount of the o-quinonediazide compound added is

preferably from 1 to 50% by weight, more preferably from 5 to 30% by weight, and particularly preferably from 10 to 30% by weight based on the total solid content of the lower layer. The substances that are thermally decomposable and can substantially decrease solubility of the alkali-soluble resin before being thermally decomposed may be used individually or as a mixture of a plurality of the compounds. When the amount of the o-quinonediazide compound is not more than 1% by weight, the image-recording property may be deteriorated. When it is not less than 50% by weight, the durability of the image area may be deteriorated and the sensitivity may be lowered.

In view of the thermal decomposing property, the onium salts are preferably used as the substance that is thermally decomposable.

It is believed that the onium salts of which the thermal decomposing property is high promote the decomposing of the substance that is thermally decomposable in the exposed area, as a result, the discrimination between the exposed and non-exposed areas is improved.

(Other additives)

In the formation of the lower and upper layers, various additives can be added in addition to the above-described components as long as the effects of the

invention are not impaired. Examples of the additives are described below.

For the purpose of intensifying the discrimination between the exposed and non-exposed areas and strengthening resistance to scratches on the surface, polymer containing as a polymerization component, a (meth)acrylate monomer unit having two or three perfluoroalkyl groups each having from 3 to 20 carbon atoms in its molecule described in JP-A-2000-187318 can be used together. These compounds may be used in the upper or lower layer, or more specifically in the upper layer.

The amount of the polymer added is preferably from 0.1 to 10% by weight, and more preferably from 0.5 to 5% by weight.

To the photosensitive lithographic printing plate precursor of the invention, a compound capable of decreasing a static friction coefficient of the surface may be added, for the purpose of imparting resistivity to scratch. Specific examples thereof include compounds containing a long chain alkyl carboxylic ester described in U.S. Patent 6,117,913. This compound may be used in the upper or lower layer, or more specifically in the upper layer when the photosensitive lithographic printing plate precursor has a multi-layer configuration.

The amount of the compound added is preferably from 0.1 to 10% by weight, and more preferably from 0.5 to 5% by weight based on the content of the layer.

Further, depending on need, the photosensitive lithographic printing plate precursor may contain a low molecular weight compound having an acid group. As the acid group, sulfonic acid, carboxylic acid and phosphoric acid groups may be mentioned. Among such compounds, compounds having a sulfonic acid group are preferred. Specifically, aromatic sulfonic acids such as p-toluenesulfonic acid, naphthalenesulfonic acid, etc. or aliphatic sulfonic acids may be mentioned.

These compounds may be incorporated in either of the lower or upper layer in case of a double-layer structure. As a preferable addition amount, the ratio to the materials composing the layer is from 0.05 to 5% by weight, more preferably from 0.1 to 3% by weight. If the ratio exceeds 5%, the solubility of each layer in the developer rises too high, giving unfavorable results.

In addition, in the present invention, a variety of dissolution inhibiting agents may be contained for the purpose of solubility adjustment. As such a dissolution inhibiting agent, disulfonic or sulfonic compounds are preferably used as shown in JP-A-11-119418. As a specific

example, 4,4'-bishydroxyphenylsulfone can be preferably used.

Such a compound may be contained in either of the lower or upper layer in case of a double-layer structure. A preferable content is from 0.05 to 20% by weight, more preferably from 0.5 to 10% by weight as the ratio occupied in the materials composing each layer.

For the purpose of further increasing the sensitivity, acid anhydrides, phenols or organic acids may be used together. Of the acid anhydrides, a cyclic acid anhydride is preferably used. Specific examples of the cyclic acid anhydride, which can be used, include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxy-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, α -phenylmaleic anhydride, succinic anhydride and pyromellitic anhydride described in U.S. Patent 4,115,128. Examples of the noncyclic acid anhydride include acetic anhydride. Examples of the phenol include bisphenol A, 2,2'-bishydroxysulfone, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4''-trihydroxytriphenylmethane and 4,4',3'',4''-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane. Examples of the organic acid include sulfonic acids,

sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphoric acid esters and carboxylic acids described in JP-A-60-88942 and JP-A-2-96755. Specific examples thereof include p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid and ascorbic acid. The amount of the acid anhydride, phenol or organic acid is preferably from 0.05 to 20% by weight, more preferably from 0.1 to 15% by weight, and particularly preferably from 0.1 to 10% by weight based on the content of the layer.

For the purposes of enhancing the stability of processing on development conditions, a nonionic surfactant described in JP-A-62-251740 and JP-A-3-208514, an amphoteric surfactant described in JP-A-59-121044 and JP-A-4-13149, a siloxane compound described in European Patent 950,517, or a copolymer comprising a fluorine-containing monomer described in JP-A-11-288093 can be added to the coating solution for each layer.

These compounds can be used for either the upper or lower layer or for both of the upper and lower layers.

Specific examples of the nonionic surfactant include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearic acid monoglyceride and polyoxyethylene nonylphenyl ether. Specific examples of the amphoteric surfactant include alkyl-di(aminoethyl)glycine, alkylpolyaminoethylglycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolinium betaine and N-tetradecyl-N,N-betaine type (for example, Amorgen K, trade name, manufactured by Dai-ich Kogyo Seiyaku Co., Ltd.).

The siloxane compound is preferably a block copolymer of dimethylsiloxane and polyalkylene oxide. Specific examples thereof include polyalkylene oxide-modified silicone, for example, DBE-224, DBE-621, DBE-712, DBP-732, DBP-534 (manufactured by Chisso Corp.) and Tego Glide 100 (manufactured by Tego A.G.).

The amount of the nonionic surfactant and the amphoteric surfactant is preferably from 0.01 to 15% by weight, more preferably from 0.05 to 5% by weight, and still more preferably from 0.1 to 0.5% by weight based on the content of the coating solution.

Each layer can contain a printing-out agent for obtaining a visible image immediately after heating upon exposure, or a dye or pigment serving as an image-coloring agent.

A representative example of the printing-out agent includes a combination of a compound capable of releasing an acid under the heating upon exposure (photo-acid releasing agent) and an organic dye capable of forming a salt. Specific examples thereof include a combination of o-naphthoquinonediazido-4-sulfonic acid halogenide and a salt-forming organic dye described in JP-A-50-36209 and JP-A-53-8128, and a combination of a trihalomethyl compound and a salt-forming organic dye described in JP-A-53-36223, JP-A-54-74728, JP-A-60-3626, JP-A-61-143748, JP-A-61-151644 and JP-A-63-58440. The trihalomethyl compound includes an oxazole compound and a triazol compound, and both compounds have excellent storage stability and provide a clear print-out image.

Examples of the image-coloring agent, which can be used, include the above-described salt-forming organic dyes and other dyes. Preferred dyes include oil-soluble dyes and basic dyes, as well as the salt-forming organic dyes. Specific examples thereof include Oil Yellow #101, Oil Yellow #103, Oil Ping #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS, Oil Black T-505 (manufactured by Orient Chemical Industry Co., Ltd.), Victoria Pure Blue, Crystal Violet lactone, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI45170B), Malachite Green (CI42000) and

Methylene Blue (CI52015). Dyes described in JP-A-62-293247 are particularly preferred. The amount of the dye added is from 0.01 to 10% by weight, preferably from 0.1 to 3% by weight, based on the total solid content of the printing plate precursor.

These compounds can be used for either the upper or lower layer or for both of the upper and lower layers.

Further, to the printing plate precursor according to the invention, a plasticizer is added, if desired, in order to impart flexibility or the like to the coating film. Examples of the plasticizer include butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, and oligomers or polymers of acrylic acid or methacrylic acid.

Each layer containing the alkali-soluble resin of the present invention can be formed by dissolving necessary ingredients in a solvent and coating the resulting solution. The solvent compositions for the upper and lower layers can be chosen depending on the constituent ingredients of each layer. The upper and lower layers can be formed by separately dissolving the constituent ingredients of each layer in a solvent, and then sequentially coating the resulting mixture on a support.

Examples of the solvent used include ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, γ -butyrolactone and toluene, however, the solvent should not be construed as being limited thereto. The solvents may be used individually or as a mixture thereof.

In the case where, after coating of the lower layer, the adjacent upper layer is coated, a solvent capable of dissolving the alkali-soluble resin in the lower layer is used as the coating solvent, mixing at the layer interface becomes unignorable. And, as an extreme case, there sometimes occurs that the structure turns to be of a single layer not of a double layer. As described above, if the adjacent two layers behave so as to mix together at the interface or be co-solubilized to give a homogeneous layer, the effects of the present invention by virtue of the double-layer structure might be unfavorably deteriorated. Accordingly, the solvent used for upper layer coating is desirably a poor solvent for the alkali-soluble resin contained in the lower layer.

The concentration of the foregoing ingredients (the solid content in total including those of additives) in the solvent used for the coating of each layer is preferably from 1 to 50% by weight.

And, as regards the coating weights (in terms of the solid content) of the upper and lower layers, which depend on use applications, a range from 0.05 to 1.0 g/m² is preferred for the upper layer, and one from 0.3 to 3.0 g/m² is preferred for the lower layer. In cases of a coating weight less than 0.05 g/m² for the upper layer, image-forming property deteriorates. When the coating weight exceeds 1.0 g/m², there arises a possibility of sensitivity lowering. Moreover, the total coating weight of the aforementioned two layers should preferably be from 0.5 to 3.0 g/m². When the total coating weight is less than 0.05 g/m², the layer property deteriorates, while, for a weight exceeding 3.0 g/m², a trend of sensitivity lowering is observed.

As the method for coating the lower and upper layers on a support, a variety of methods can be adopted. For example, bar coater coating, rotation coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, roll coating, etc. can be mentioned.

In each layer of the present invention, for the purpose of improving coating property, a surfactant such

as, for example, fluorine-containing surfactants as set forth in JP-A-62-170950 can be incorporated. A preferable range of added amount is from 0.01 to 1% by weight, more preferably from 0.05 to 0.5% by weight of the total solid content of the layer to which the surfactant is incorporated.

After a lower layer is coated on a support, and then an upper layer is coated thereon, drying is conducted for each layer, respectively. As the drying method, ordinary, well-known ones are adopted. For example, a countercurrent heating method wherein a hot air stream is blown onto the support on which the coating has been made, a radiation heating method set forth in JP-A-60-149871 wherein drying is carried out with the heat radiated from heating plates arranged above and under the support, and a conduction heating method set forth in JP-A-60-21334 and JP-A-60-62778 wherein a heating medium is passed through the inside of a roller, with which the support is brought into contact to achieve drying by the heat conduction from the roller surface, etc. may be adopted.

With respect to the developing property of a photo-sensitive lithographic printing plate precursor, if the drying condition is severe, the electro-conductivity of the developer capable of image formation tends to be high (the developing property becoming low), and if the drying

condition is mild, the electro-conductivity of the developer capable of image formation tends to be low (the developing property becoming high). Selection of desirable drying conditions can be achieved by the control of conditions such as blowing air temperature, blowing air quantity, air blowing direction, the temperature and material of the contacted heat medium, etc.

It is desirable that the residual solvent in the lower layer is scarce immediately before the upper layer coating. The residual solvent in the lower layer is preferably 80 mg/m² or less, more preferably 60 mg/m² or less.

In case where a lower layer and an upper layer thereon are provided on a support, the upper layer is coated after, following the drying of the lower layer, the temperature of the support is once lowered to a predetermined level.

In the present invention, the drying method may be any of the above-mentioned ones, but the temperature of the support immediately before the coating of the coating mixture for the upper layer (i.e., at the moment when the coating mixture is brought into contact with the support) must be 40°C or lower, more preferably from 22 to 38°C. By starting coating under a condition of keeping the support temperature at such a low range, not only scratch

resistance and the discrimination between the image area and the non-image area can be secured but also printing durability improves noticeably.

As the method of lowering the support temperature, there can be mentioned a cold air blowing method, one in which a cooling medium is passed through the inside of a roller, with which the support is brought into contact, and in which the support is cooled by the heat conduction from the roller surface, a method of passing the support through a low temperature environment such as water, one based on cooling with a latent heat of vaporization by spraying a liquid having a low boiling point, etc. Among those, the cold air blowing method is preferred. The temperature of the cold air is preferably set at 30°C or lower. More preferably, the temperature is 20°C or lower, and particularly preferably 10°C or lower.

[Support]

The support for use in the invention includes a dimensionally stable plate material having necessary strength and durability. Examples of the support include paper, paper laminated with plastic (for example, polyethylene, polypropylene or polystyrene), a metal plate (for example, an aluminum, zinc or copper plate), a plastic film (for example, a cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose

butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate or polyvinyl acetal film), and paper or plastic film having laminated or deposited thereon the metal described above.

The support for use in the photosensitive lithographic printing plate precursor of the invention is preferably a polyester film or an aluminum plate. Among them, the aluminum plate is particularly preferred, since it is dimensionally stable and relatively inexpensive. The aluminum plate is preferably a pure aluminum plate or an alloy plate mainly comprising aluminum and containing a trace amount of foreign element. A plastic film having laminated or deposited thereon aluminum may also be used. Examples of the foreign element contained in the aluminum alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium. The content of foreign element in the alloy is at most 10% by weight. In the invention, particularly preferred aluminum is pure aluminum but since perfectly pure aluminum is difficult to produce in view of the refining technique, the aluminum may contain a trace amount of foreign element.

The aluminum plate for use in the invention is not particularly limited on the composition and an aluminum plate conventionally known and commonly used can be

appropriately used. The thickness of the aluminum plate for use in the invention is approximately from 0.1 to 0.6 mm, preferably from 0.15 to 0.4 mm, and particularly preferably from 0.2 to 0.3 mm.

Prior to surface roughening of an aluminum plate, a degreasing treatment using, for example, a surfactant, an organic solvent or an aqueous alkaline solution is performed, if desired, in order to remove the rolling oil on the surface. The surface roughening treatment of the aluminum plate is performed by various methods, for example, a method of mechanically roughening the surface, a method of electrochemically dissolving and roughening the surface or a method of chemically dissolving selectively the surface. In the mechanical roughening method, a known method, for example, ball graining, brush graining, blast graining or buff graining may be used. The electrochemical surface roughening method includes a method of performing the treatment by applying an alternating current or direct current through an electrolytic solution containing hydrochloric acid or nitric acid. A method using these two treatments in combination described in JP-A-54-63902 may also be used. After such surface roughening, the aluminum plate is, if desired, subjected to an alkali etching treatment and a neutralization treatment and then, if desired, to an

anodization treatment in order to enhance the water retentivity or abrasion resistance on the surface. The electrolyte, which can be used in the anodization treatment of the aluminum plate, includes various electrolytes capable of forming a porous oxide film, and sulfuric acid, phosphoric acid, oxalic acid, chromic acid or a mixed acid thereof is ordinarily used. The concentration of the electrolyte is appropriately determined depending on the kind of electrolyte.

The conditions of anodization treatment vary depending on the electrolyte used and therefore, cannot be indiscriminately specified, however, suitable conditions are ordinarily such that the concentration of electrolyte is from 1 to 80% by weight, the solution temperature is from 5 to 70°C, the current density is from 5 to 60 A/dm², the voltage is from 1 to 100 V, and the electrolysis time is from 10 seconds to 5 minutes. When the amount of anodic oxide film is less than 1.0 g/m², insufficient printing durability may result or the non-image area of lithographic printing plate is readily scratched to cause so-called "scratch stain", namely, adhesion of ink to the scratched part at the printing. After the anodization treatment, the aluminum surface is, if desired, subjected to a hydrophilization treatment. Examples of the hydrophilization treatment for use in the printing plate

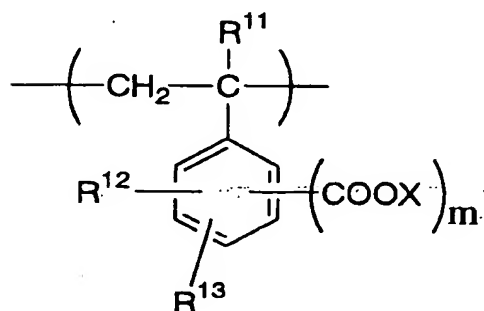
precursor of the invention include a method of using an alkali metal silicate (for example, an aqueous sodium silicate solution) described in U.S. Patents 2,714,066, 3,181,461, 3,280,734 and 3,902,734. According to the method, the support is immersed or electrolyzed in an aqueous sodium silicate solution. Further, a method of treating the support with potassium fluorozirconate described in JP-B-36-22063 or with polyvinylphosphonic acid described in U.S. Patents 3,276,868, 4,153,461 and 4,689,272 may be used.

The photosensitive lithographic printing plate precursor of the invention comprises at least the above-described upper and lower layers on the support but, if desired, an undercoat layer may be provided between the lower layer and the support.

For components of the undercoat layer, various organic compounds are used and examples thereof include carboxymethyl cellulose; dextrin; gum arabic; phosphonic acids having an amino group, e.g., 2-aminoethylphosphonic acid; organic phosphonic acids, e.g., phenylphosphonic acid, naphthylphosphonic acid, alkyl phosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid, each of which may have a substituent; organic phosphoric acids, e.g., phenylphosphoric acid, naphthylphosphoric acid,

alkylphosphoric acid and glycerophosphoric acid, each of which may have a substituent; organic phosphinic acids, e.g., phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid, each of which may have a substituent; amino acids, e.g., glycine and β -alanine; and hydrochlorides of amines having a hydroxy group, e.g., hydrochloride of triethanolamine. The compounds may be used as a mixture of two or more thereof.

In addition, an undercoat layer containing at least one compound selected from the organic polymer compounds having the structural unit represented by the following formula is also preferable.



In the formula, R^{11} represents a hydrogen atom, a halogen atom or an alkyl group, R^{12} and R^{13} each independently represent a hydrogen atom, a hydroxy group, a halogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, $-\text{OR}^{14}$, $-\text{COOR}^{15}$, $-\text{CONHR}^{16}$, $-\text{COR}^{17}$ or $-\text{CN}$, or R^{12} and R^{13} may combine together to form a ring, R^{14} to R^{17} each independently represent an

alkyl group or an aryl group, X represents a hydrogen atom, a metal atom, $\text{NR}^{18}\text{R}^{19}\text{R}^{20}\text{R}^{21}$, R^{18} to R^{21} each independently represent a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, or R^{18} and R^{19} may combine together to form a ring, and m represents an integer of 1 to 3.

The undercoat layer can be provided by the following methods. Specifically, there are a method of dissolving the above-described organic compound in water, an organic solvent, e.g., methanol, ethanol or methyl ethyl ketone, or a mixed solvent thereof, coating the resulting solution on an aluminum plate and drying it to provide the undercoat layer, and a method of dissolving the organic compound in water, an organic solvent, e.g., methanol, ethanol or methyl ethyl ketone, or a mixed solvent thereof, immersing an aluminum plate in the resulting solution to adsorb the compound, washing the aluminum plate with water or the like, and drying it to provide the organic undercoat layer. In the former method, the solution containing the organic compound in a concentration of 0.005 to 10% by weight can be coated by various methods. In the latter method, the concentration of the solution is from 0.01 to 20% by weight, preferably from 0.05 to 5% by weight, the immersion temperature is from 20 to 90°C, preferably from 25 to 50°C, and the immersion time is from

0.1 second to 20 minutes, preferably from 2 seconds to 1 minute. The solution used may also be adjusted its pH to a range of from 1 to 12 with a basic substance, for example, ammonia, triethylamine or potassium hydroxide or an acidic substance, for example, hydrochloric acid or phosphoric acid. Moreover, a yellow dye may be added to the solution in order to improve the tone reproducibility of the photosensitive lithographic printing plate precursor.

The coverage of the undercoat layer is suitably from 2 to 200 mg/m², and preferably from 5 to 100 mg/m². When the coverage of the undercoat layer is not more than 2 mg/m² or not less than 200 mg/m², favorable printing durability can not be obtained.

[Plate-making and printing]

As the most general manner, the photosensitive lithographic printing plate precursors prepared in the above-described manner are shipped, transported and stocked in the product form in which the precursors are stacked with a sheet of paper inserted between the adjacent photo-sensitive lithographic printing plate precursors. As a typical manner for plate making and printing, a pair consisting of an inserted sheet of paper and a plate precursor is secured at an auto-loader by means of the auto-loader, transported, and mounted to be

fixed at the position where plate making is conducted, and thereafter the inserted sheet of paper is removed. But the use manner should not be limited to the above.

To the plate precursor from which the inserted paper has been removed, image exposure and development processing are carried out.

As the light source of the actinic light used for image exposure, those having emission light wavelengths in near infrared to infrared regions are preferred. And they need not always be of scanning type, but may be of plane (dioptric) exposure type. However, the scanning-type exposure using a solid laser or semi-conductor laser is preferred. As the emission light wavelength, 760 to 1080 nm are preferred.

The developer applicable to the photo-sensitive lithographic printing plate precursor of the present invention is one having a pH in the range from 9.0 to 14.0, preferably from 12.0 to 13.5. As the developer (hereinafter, the term developer being used also for the replenisher), the conventionally known aqueous alkaline solutions can be used. For example, inorganic alkaline salts such as sodium silicate or potassium silicate, tertiary sodium phosphate, potassium phosphate or ammonium phosphate, secondary sodium phosphate, potassium phosphate or ammonium phosphate, sodium carbonate, potassium

carbonate or ammonium carbonate, sodiumhydrogen carbonate, potassium hydrogen carbonate or ammonium hydrogencarbonate, sodium borate, potassium borate or ammonium borate, sodium hydroxide, potassium hydroxide, ammonium hydroxide or lithium hydroxide, etc. are mentioned. Moreover, organic alkaline agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, pyridine, etc. are mentioned. Such an aqueous alkaline solution may be used individually as a single component or in combination of two or more.

Among the above-cited aqueous alkaline solution, as the "developer with which the effect of the present invention is exhibited, one is an aqueous solution, called "silicate developer" and having a pH not lower than 12, containing an alkali silicate as a base or containing the alkali silicate obtained by mixing a base with a silicon compound, while another more preferable one is a so-called "non-silicate developer" which is free of alkali silicate, but contains a non-reducing sugar (an organic compound having a buffer action) and a base.

In the former, the developing property of the aqueous solution of an alkali metal silicate can be controlled by the ratio of silicon oxide SiO_2 to an alkali metal oxide M_2O (generally represented by the molar ratio of $[\text{SiO}_2]/[\text{M}_2\text{O}]$ and their concentrations. Thus, for example, as set forth in JP-A-54-62004, a developer is an aqueous sodium silicate solution in which the molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ is 1.0 to 1.5 (i.e., $[\text{SiO}_2]/[\text{Na}_2\text{O}] = 1.0$ to 1.5) and in which the content of SiO_2 is 1 to 4% by weight. Or another preferably used developer is an aqueous alkali metal silicate solution in which the molar ratio of $[\text{SiO}_2]/[\text{M}]$ is 0.5 to 0.75 (i.e., $[\text{SiO}_2]/[\text{M}_2\text{O}] = 1.0$ to 1.5), in which the content of SiO_2 is 1 to 4% by weight, and in which at least 20% of potassium based on the gram atom number of the total alkali metal present in the developer as set forth in JP-A-57-7427.

Further, the so-called "non-silicate developer" free of alkali silicate and containing a non-reducing sugar and a base is more preferably applied to the development of the lithographic printing plate precursor of the present invention. When the development processing is conducted for the lithographic printing plate precursor by using this type of developer, not only the surface of the photosensitive layer is not deteriorated, but also the ink-attracting property of the photo-sensitive layer can

be maintained in a desirable condition. And, generally speaking, lithographic printing plate precursors exhibit a narrow development latitude, causing image line width, etc. to largely vary depending on the pH of the developer. But, since the non-silicate developer contains a non-reducing sugar, which has a buffer action of suppressing pH variation, it is advantageous compared with the case of using a silicate-containing developer. Further, since the non-reducing sugar tends to less contaminate, in comparison with silicates, an electro-conductivity sensor, a pH sensor, etc., all being used for the control of the developer activity, the non-silicate developer is advantageous in this aspect, too. Still further, the effect of enhancing the discrimination between the image and non-image areas is noticeable. This effect is presumed to be due to the fact that the contact with (penetration of) the developer, which is significant for discrimination as well as film property maintenance, is mild in the present invention, thus leading to the ease with which the exposed area is differentiated from the unexposed area.

The aforementioned non-reducing sugar implies saccharide compounds having no free aldehyde or ketone group, exhibiting no reducing nature, and is classified to trehalose-type oligosaccharides in which reducing groups

bind together, glycosides in which the reducing group of a saccharide is bonded to a non-saccharide, and sugar-alcohols resulting from the reduction of a saccharide by hydrogenation. Each of these compounds can be preferably used for the present invention. By way of precaution, the non-reducing sugars set forth in JP-A-8-305039 can be favorably used.

Examples of the trehalose-type oligosaccharide include saccharose and trehalose. Examples of the glycosides include alkyl glycoside, phenol glycoside and mustard oil glycoside. Examples of the sugar-alcohol include D,L-arabitol, ribitol, xylitol, D,L-sorbitol, D,L-mannitol, D,L-iditol, D,L-talitol, dulcitol and allodulcitol. In addition, maltitol obtained by hydrogenation of disaccharide, and a reduction product (reduced starch syrup) obtained by hydrogenation of oligosaccharide may be preferably used. Among the non-reducing sugars, sugar-alcohol and saccharose are preferred, and D-sorbitol, saccharose and reduced starch syrup are more preferred because they have a buffering action in an appropriate pH region and are priced lower.

The non-reducing sugars may be used individually or in combination of two or more thereof. The amount of the non-reducing sugar in the developing solution is preferably from 0.1 to 30% by weight, and more preferably

from 1 to 20% by weight. When the aforementioned amount is below 0.1% by weight, exertion of sufficient buffer action tends to be difficult. And when it exceeds 30% by weight, such a high concentration becomes difficult to achieve, and the manufacturing cost also tends to be high.

The base used in combination with the non-reducing sugars can be appropriately selected from conventionally known alkali agents. Examples of the alkali agent include inorganic alkali agents, for example, sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium phosphate, dipotassium phosphate, diammonium phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate or ammonium borate, and potassium citrate, tripotassium citrate and sodium citrate.

Other examples of the alkali agent, which can be preferably used, include organic alkali agents, for example, monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine and pyridine.

The base compounds may be used individually or in combination of two or more thereof. Among the compounds, sodium hydroxide and potassium hydroxide are preferred.

As the non-silicate developer, instead of the combination of the non-reducing sugars and the base compounds, alkali metal salts of non-reducing sugar are used as main component.

In addition, in combination with the aforementioned non-silicate developer, an alkaline buffer solution containing a weak acid other than the aforementioned non-reducing sugar and a strong base can be adopted. As the aforementioned weak acid, those having a dissociation constant (pK_a) of from 10.0 to 13.2 are preferred, and can be chosen from the compounds set forth in, for example, "Ionization Constants of Organic Acids in Aqueous Solution" published by Pergamon Press, etc.

Specifically, alcohols such as 2,2,3,3-tetrafluoropropanol-1, trifluoroethanol, trichloroethanol, etc., aldehydes such as pyridine-2-aldehyde, pyridine-4-aldehyde, etc., compounds having a phenolic hydroxy group such as salicylic acid, 3-hydroxy-2-naphthoic acid, catechol, gallic acid, sulfosalicylic acid, 3,4-dihydroxysulfonic acid, 3,4-dihydroxybenzoic acid, hydroquinone (ibid, 11.56), pyrogallol, o-, m- or p-cresol, resorcinol, etc., oximes such as acetoxime, 2-

hydroxybenzaldehydioxime, dimethylglyoxime, ethandiamidedioxime, acetophenoneoxime, etc., nucleic acid-related substances such as adenosine, inosine, guanine, cytosine, hypoxanthine, xanthine, etc., and in addition, diethylaminomethylphosphinic acid, benzimidazole, barbituric acid, etc. can be mentioned.

In the developing solution and the replenisher, a variety of surfactants and organic solvents may be added, if desired, for the purpose of accelerating or inhibiting the development, dispersing the development scum, or enhancing the ink-receptivity of the image area of printing plate. Preferred examples of the surfactant include anionic, cationic, nonionic and amphoteric surfactants. Furthermore, the developing solution and/or replenisher may contain, if desired, a reducing agent, for example, hydroquinone, resorcinol or a sodium salt or potassium salt of an inorganic acid (e.g., sulfurous acid, hydrogen sulfurous acid), an organic carboxylic acid, a defoaming agent and a water softening agent.

The lithographic printing plate precursor developed using the above-described developing solution and replenisher is subjected to an after-treatment with washing water, a rinsing solution containing a surfactant or the like, or a desensitizing solution containing gum arabic or a starch derivative. These treatments can be

used in various combinations for the after-treatment of the heat-sensitive lithographic printing plate precursor of the invention.

In plate-making and printing industries, automatic developing processors are widely used for consistent operation of developing exposed photo-sensitive lithographic printing plate precursors. Such an automatic developing processor, which generally comprises a developing unit and a post-processing unit, and comprises an apparatus for transporting printing plates, tanks and spraying apparatuses for individual processing solutions, conducts, along with horizontal transportation of an exposed printing plate precursor, development processing by spraying each pumped up processing solution from spray nozzles. Moreover, recently, a processing method is known in which a printing plate precursor is immersed and transported, by means of immersed guide rolls, through processing solution tanks filled with processing solutions. Under such automatic processing, processing can be performed under replenishing the replenisher for each processing solution depending on the processed amount or operating period, etc.

The infrared photosensitive lithographic printing plate precursor has adaptability to the processing by the aforementioned automatic processor. Further, the so-

called one-time use processing method can be applied in which, for each photo-sensitive lithographic printing plate precursor, a fresh volume of the processing solution is supplied.

Furthermore, to the photosensitive lithographic printing plate precursor of the invention, a so-called disposable processing system can also be applied, wherein development processing is carried out by supplying a substantially fresh developing solution per sheet of the exposed photosensitive lithographic printing plate precursor, besides the processing by an automatic developing machine with a replenishing system as described above.

In the case where a lithographic printing plate obtained from the photosensitive lithographic printing plate precursor of the invention through image exposure, development, water washing and/or rinsing and/or gumming has an unnecessary image area, elimination of the unnecessary image area is carried out. Such elimination is preferably performed by a method described, for example, in JP-B-2-13293, where a eliminating solution is applied to the unnecessary image area, allowed to stand for a predetermined time and thereafter, washed with water. However, a method described in JP-A-59-174842, where the unnecessary image area is irradiated with an active beam

guided by an optical fiber and then subjected to development is also utilized.

The thus-obtained printing plate is, if desired, coated with a desensitizing gum and then can be used for printing. However, when a lithographic printing plate having higher printing durability is desired, the printing plate is subjected to a burning treatment. In the case of burning the lithographic printing plate, the plate before the burning is preferably treated with a plate burning conditioner described, for example, in JP-B-61-2518, JP-B-55-28062, JP-A-62-31859 and JP-A-61-159655.

The treatment may be performed by a method of applying the plate burning conditioner on the lithographic printing plate using a sponge or an absorbent cotton impregnated with the plate burning conditioner, a method of applying the plate burning conditioner by immersing the lithographic printing plate in a vat filled with the plate burning conditioner, or a method of applying the plate burning conditioner using an automatic coater. When the amount of plate burning conditioner applied is made uniform by a squeegee or a squeegee roller after the application, more preferred results can be obtained.

The amount of the plate burning conditioner applied is ordinarily from 0.03 to 0.8 g/m² (dry weight). The lithographic printing plate applied with the plate burning

conditioner is dried, if desired, and then heated at a high temperature by a burning processor (for example, a burning processor "BP-1300" commercially available from Fuji Photo Film Co., Ltd.). The heating temperature and the heating time are preferably from 180 to 300°C and from 1 to 20 minutes, respectively, though these may be varied depending on the components constituting the image.

The lithographic printing plate after the burning treatment can be subjected, if desired, to conventional treatment, for example, water washing and gumming, however, in the case where a plate burning conditioner containing a water-soluble polymer compound or the like is used, a so-called desensitizing treatment, for example, gumming can be omitted. The lithographic printing plate obtained through such treatments is mounted on an offset printing machine and used for printing of a large number of sheets.

The invention is described in greater detail with reference to the following examples, but the invention should not be construed as being limited thereto.

[Example]

[Preparation examples of support]

(Preparation of Support 1)

An aluminum plate having a thickness of 0.24 mm (made of aluminum alloy containing 0.06% by weight of Si, 0.30% by weight of Fe, 0.014% by weight of Cu, 0.001% by

weight of Mn, 0.001% by weight of Mg, 0.001% by weight of Zn, 0.03% by weight of Ti, and the balance of Al and unavoidable impurities) was continuously subjected to the surface treatments described below.

Mechanical graining of the aluminum plate was carried out using rotating roller-form nylon brushes while supplying a suspension of abrasives (silica sand) in water having a specific gravity of 1.12 to the surface of the aluminum plate as an abrasive slurry. The aluminum plate was then subjected to an etching treatment by spraying a solution having a sodium hydroxide concentration of 2.6% by weight, an aluminum ion concentration of 6.5% by weight and a temperature of 70°C to dissolve 6 g/m² of the aluminum plate, followed by washing with water by spraying. Further, the aluminum plate was subjected to a desmut treatment by spraying an aqueous solution having a nitric acid concentration of 1% by weight (containing 0.5% by weight of aluminum ion) and a temperature of 30°C, followed by washing with water by spraying. Then, using an alternating current of 60 Hz, an electrochemical graining treatment was continuously carried out. The electrolyte used was an aqueous solution of 10 g/liter of nitric acid (containing 5 g/liter of aluminum ion and 0.007% by weight of ammonium ion) and the temperature was 80°C. After washing with water, the aluminum plate was

subjected to an etching treatment by spraying a solution having a sodium hydroxide concentration of 26% by weight and an aluminum ion concentration of 6.5% by weight at 32°C to dissolve 0.20 g/m² of the aluminum plate, followed by washing with water by spraying. Then, the aluminum plate was subjected to a desmut treatment by spraying an aqueous solution having a sulfuric acid concentration of 25% by weight (containing 0.5% by weight of aluminum ion) and a temperature of 60°C, followed by washing with water by spraying.

The aluminum plate was then subjected to an anodizing treatment using an anodizing apparatus of a two-stage feeding electrolytic treatment method. As an electrolyte supplied to the electrolytic parts, sulfuric acid was used. Thereafter, washing with water was performed by spraying. The final amount of the oxidized film formed was 2.7 g/m².

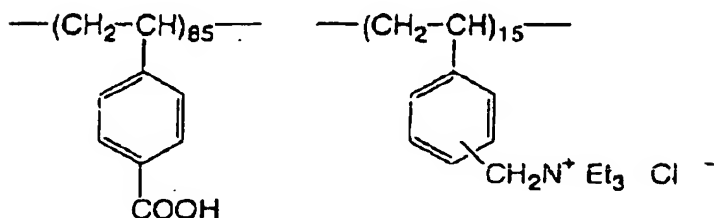
The aluminum plate subjected to the anodizing treatment was immersed in an aqueous solution of 1% by weight 3# sodium silicate and a temperature of 30°C for 10 seconds, whereby an alkali metal silicate treatment (silicate treatment) was carried out. Then, washing with water was performed by spraying.

On the aluminum plate after the silicate treatment obtained above, the undercoat solution having the composition described below was coated, followed by drying

at 80°C for 15 seconds to form a undercoat layer having a dry coating coverage of 15 mg/m², whereby Support D was prepared.

<Composition of undercoat solution >

Compound described below	0.3 g
Methanol	100 g
Water	1 g



Molecular weight 28,000

(Preparation of Support 2)

An aluminum plate same as used in Preparation of Support 1 was continuously subjected to the surface treatments described below.

The aluminum plate was continuously subjected to an electrochemical graining treatment using an alternating current of 60 Hz. The electrolyte used was an aqueous solution of 10 g/liter of nitric acid (containing 5 g/liter of aluminum ion and 0.007% by weight of ammonium ion) and the temperature was 80°C. After washing with water, the aluminum plate was subjected to an etching treatment by spraying a solution having a sodium hydroxide

concentration of 26% by weight and an aluminum ion concentration of 6.5% by weight at 32°C to dissolve 0.20 g/m² of the aluminum plate, followed by washing with water by spraying. Then, the aluminum plate was subjected to a desmut treatment by spraying an aqueous solution having a sulfuric acid concentration of 25% by weight (containing 0.5% by weight of aluminum ion) and a temperature of 60°C, followed by washing with water by spraying.

On the aluminum plate subjected to the electrochemical graining treatment were conducted the anodizing treatment, silicate treatment and coating of undercoat solution in the same manner as in Preparation of Support 1, whereby Support 2 was prepared.

(Preparation of Support 3)

An aluminum plate (JIS A1050) having a thickness of 0.3 mm was subjected to an etching treatment with a solution having a sodium hydroxide concentration of 30 g/liter and an aluminum ion concentration of 10 g/liter at a solution temperature of 60°C for 10 seconds, washing with running water, neutralization and cleaning with a solution having a nitric acid concentration of 10 g/l, and washing with water. The aluminum plate was then subjected to an electrochemical graining treatment in an aqueous solution having a hydrogen chloride concentration of 15 g/l, an aluminum ion concentration of 10 g/liter and a

solution temperature of 30°C using an alternating current with a sinusoidal waveform under the condition of applied voltage $V_a = 20V$ at electric charge of 500 C/dm^2 , washing with water, an etching treatment with a solution having a sodium hydroxide concentration of 30 g/liter and an aluminum ion concentration of 10 g/liter at a solution temperature of 40°C for 10 seconds, and washing with running water. The aluminum plate was then subjected to a desmut treatment in an aqueous sulfuric acid solution having a sulfuric acid concentration of 15% by weight and a solution temperature of 30°C, followed by washing with water. Further, the aluminum plate was subjected to an anodizing treatment using a direct current in a 10% by weight aqueous sulfuric acid solution having a solution temperature of 20°C at a current density of 6 A/dm^2 so as to form an anodizing film having an amount of 2.5 g/m^2 , followed by washing with water and drying. Thereafter, the aluminum plate was treated with an aqueous solution of 2.5% by weight sodium silicate at a temperature of 30°C for 10 seconds, thereby preparing a support. The centerline average roughness (R_a) of the support was measured using a stylus having a diameter of $2 \text{ }\mu\text{m}$ and found to be $0.48 \text{ }\mu\text{m}$.

On the aluminum plate after the silicate treatment obtained above, the undercoat solution described above was

coated (at a dry coating coverage of 17 mg/m^2) in the same manner as in Preparation of Support 1, whereby Support 3 was prepared.

(Preparation of Support 4)

Each of the steps (a) to (1) was performed in this order to prepare Support 4.

(a) Mechanical graining treatment

An aluminum plate of JIS A1050 having a thickness of 0.3 mm was subjected to mechanical graining using rotating roller-form nylon brushes while supplying a suspension of abrasives (silica sand) in water having a specific gravity of 1.12 to the surface of the aluminum plate as an abrasive slurry. The mean grain size of the abrasives was $8 \mu\text{m}$ and the maximum grain size thereof was $50 \mu\text{m}$. The material of bristle of the nylon brush was Nylon 6, 10, the length of the bristle was 50 mm, and the diameter of the bristle was 0.3 mm. The nylon brush was prepared by making many holes in the wall of a stainless steel-made cylinder having a diameter of 300 mm and bristles were planted in the holes closely. Three rotary brushes were used. The distance of two supporting rollers (diameter of 200 mm) under the brushes was 300 mm. The brushes pressed the aluminum plate by the brush rollers until the load of a driving motor rotating the brushes became 7 kW plus to the load before pressing the aluminum plate by the brush

rollers. The rotating direction of the brushes was same as the moving direction of the aluminum plate. The rotation number of the brushes was 200 rpm.

(b) Alkali etching treatment

The aluminum plate treated as described above was subjected to an etching treatment by spraying an aqueous sodium hydroxide solution (sodium hydroxide concentration: 26% by weight; aluminum ion concentration: 6.5% by weight) having a temperature of 70°C to dissolve 6 g/m² of the aluminum plate. Thereafter, water washing was carried out by spraying well water.

(c) Desmut treatment

The desmut treatment was carried out by spraying an aqueous solution having a nitric acid concentration of 1% by weight (containing 0.5% by weight of aluminum ion) having a temperature of 30°C, and thereafter the aluminum plate was washed by spraying water. As the aqueous nitric acid solution used in the desmut treatment, waste liquid from the step of carrying out electrochemical graining using alternating current in an aqueous nitric acid solution was employed.

(d) Electrochemical graining treatment

Using an alternating current of 60 Hz, an electrochemical graining treatment was continuously carried out. The electrolyte used was an aqueous solution

of 10.5 g/liter of nitric acid (containing 5 g/liter of aluminum ion) and the temperature was 50°C. The electrochemical graining treatment was conducted using an alternating current source which provides a trapezoidal rectangular wave alternating current of 0.8 msec in time TP for the current to reach its peak from zero and 1:1 in duty ratio and using a carbon electrode as a counter electrode. A ferrite was used as an auxiliary anode. As an electrolysis vessel, a radial cell type was used.

The current density was 30 A/dm² in the peak value of the electric current and the quantity of electricity was 220 C/dm² in terms of the total quantity of electricity during the aluminum plate functioning as an anode. To the auxiliary electrode, 5% of the electric current from the electric source was provided.

Thereafter, water washing was carried out by spraying well water.

(e) Alkali etching treatment

The aluminum plate was subjected to an etching treatment by spraying an aqueous solution having a sodium hydroxide concentration of 26% by weight and an aluminum ion concentration of 6.5% by weight at 32°C to dissolve 0.20 g/m² of the aluminum plate, whereby the smut components mainly composed of aluminum hydroxide formed in the electrochemical graining using an alternating current

in the preceding step were removed and also, the edge portions of pits formed were dissolved to make the edge portions smooth. Thereafter, water washing was carried out by spraying well water.

(f) Desmut treatment

The desmut treatment was carried out by spraying an aqueous solution having a sulfuric acid concentration of 15% by weight (containing 4.5% by weight of aluminum ion) having a temperature of 30°C, and thereafter, water washing was carried out by spraying well water. As the aqueous nitric acid solution used in the desmut treatment, waste liquid from the step of carrying out electrochemical graining using alternating current in an aqueous nitric acid solution was employed.

(g) Electrochemical graining treatment

Using an alternating current of 60 Hz, an electrochemical graining treatment was continuously carried out. The electrolyte used was an aqueous solution of 7.5 g/liter of hydrochloric acid (containing 5 g/liter of aluminum ion) and the temperature was 35°C. The electrochemical graining treatment was conducted using an alternating current source which provides a rectangular wave alternating current and using a carbon electrode as a counter electrode. A ferrite was used as an auxiliary

anode. As an electrolysis vessel, a radial cell type was used.

The current density was 25 A/dm^2 in the peak value of the electric current and the quantity of electricity was 50 C/dm^2 in terms of the total quantity of electricity during the aluminum plate functioning as an anode.

Thereafter, water washing was carried out by spraying well water.

(h) Alkali etching treatment

The aluminum plate was subjected to an etching treatment by spraying an aqueous solution having a sodium hydroxide concentration of 26% by weight and an aluminum ion concentration of 6.5% by weight at 32°C to dissolve 0.10 g/m^2 of the aluminum plate, whereby the smut components mainly composed of aluminum hydroxide formed in the electrochemical graining using alternating current in the preceding step were removed and also, the edge portions of pits formed were dissolved to make the edge portions smooth. Thereafter, water washing was carried out by spraying well water.

(i) Desmut treatment

The desmut treatment was carried out by spraying an aqueous solution having a sulfuric acid concentration of 25% by weight (containing 0.5% by weight of aluminum ion)

having a temperature of 60°C, and thereafter, water washing was carried out by spraying well water.

(j) Anodizing treatment

The anodizing treatment was carried out using sulfuric acid as an electrolyte. The electrolyte had a sulfuric acid concentration of 170 g/liter (containing 0.5% by weight of aluminum ion) and the temperature was 43°C. Thereafter, water washing was carried out by spraying well water.

The current density was about 30 A/dm². The final amount of the oxidized film formed was 2.7 g/m².

(k) Silicate treatment

The silicate treatment was conducted in the same manner as in Preparation of Support D. The amount of silicate attached was 3.5 mg/m².

(l) Formation of undercoat layer

The coating of the undercoat solution described above was conducted in the same manner as in Preparation of Support 1. A coating coverage of the undercoat layer after drying was 15 mg/m².

Examples 1 to 37 and Comparative Examples 1 to 3

[Preparation of photosensitive lithographic printing plate precursor]

On the support obtained as described above, Coating solution 1 for lower layer having the composition shown

below was coated and dried at 130°C for 50 seconds using PERFECT OVEN PH200 manufactured by TABAI Corp. by setting Wind Control 7 to provide a lower layer having a dry coated amount of 0.85/m². Then, Coating solution 1 for upper layer having the composition shown below was coated so as to have a dry coated amount of 0.25 g/m². The drying was conducted under condition of 140°C for one minute.

Kinds of copolymers containing a monomer unit represented by formula (I) and amounts thereof added to the coating solutions used in Examples 1 to 37 and Comparative Examples 1 to 3 are shown in Table 1 below.

(Coating solution 1 for lower layer)

N-(4-Aminosulfonylphenyl)methacryl-	2.133 g
amide/acrylonitrile/methyl methacrylate	
copolymer (36/34/30% by weight; weight average	
molecular weight: 50,000; acid value: 2.65)	

Cyanine dye A (having the structure shown	0.109 g
above)	

4,4'-Bishydroxyphenylsulfone	0.126 g
cis- Δ^4 -Tetrahydrophthalic anhydride	0.190 g
p-Toluenesulfonic acid	0.008 g

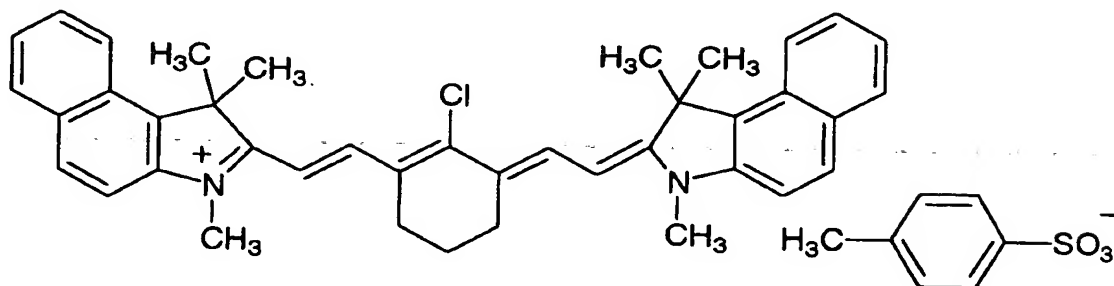
3-Methoxy-4-diazodiphenylamine	0.030 g
hexafluorophosphate	

Compound obtained by replacing	0.100 g
counter ion of Ethyl Violet with	
6-hydroxy-2-naphthalenesulfonate	

Megafac F176 (manufactured by DAINIPPON	0.035 g
INK & CHEMICALS, INC.)	
(Fluorine-containing surfactant for	
improving coated surface state)	

Methyl ethyl ketone	25.38 g
1-Methoxy-2-propanol	13.0 g
γ -Butyrolactone	13.2 g

Cyanine dye A



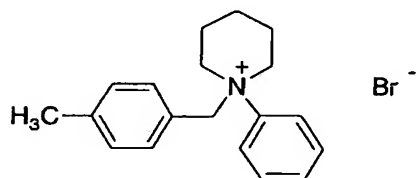
(Coating solution 1 for upper layer)

m,p-Cresol novolak resin (m/p ratio = 6/4; 0.3478 g
weight average molecular weight: 4,500;
containing 0.8% by weight of unreacted cresol)

Copolymer according to the invention (kind and amount
as described in Table 2)

Cyanine dye A (having the structure shown 0.0192 g
above)

Ammonium compound having the structure 0.0115 g
shown below



Megafac F176 (20%) (manufactured by 0.022 g
DAINIPPON INK & CHEMICALS, INC.)
(Surfactant for improving coated
surface state)

1-Methoxy-2-propanol 13.07 g

Methyl ethyl ketone 6.79 g

In the comparative examples, methacrylic acid/methyl methacrylate copolymer was used in place of the copolymer according to the invention as shown in Table 1.

[Evaluation of development latitude]

A test pattern was imagewise drawn on each of the lithographic printing plate precursors at a beam intensity of 9 W and a drum rotation speed of 150 rpm using Trendsetter manufactured by Creo Inc. The exposed lithographic printing plate precursor was developed using PS Processor LP940H manufactured by Fuji Photo film Co., Ltd., to which a developing solution prepared by diluting Developer DT-2R manufactured by Fuji Photo film Co., Ltd. using 5 parts by volume of water per one part by volume of the developer (hereinafter simply referred to as "1:5 diluted solution") and introducing carbon dioxide gas into the solution until electric conductivity reaching 37 mS/cm, and a solution prepared by diluting Finisher FG-1 manufactured by Fuji Photo film Co., Ltd. using one part by volume of water per one part by volume of the finisher ("1:1 diluted solution") had been charged, at a solution temperature of 30°C for a developing time of 12 seconds. Then, to the developing solution was added an appropriate amount of DT-2R (1:5 diluted solution) to adjusted its electric conductivity to 39 mS/cm and using the resulting

developing solution, the lithographic printing plate precursor imagewise drawn a test pattern in the same manner as described above was developed. The same procedures as above were repeated with increasing the electric conductivity by 2 mS/cm each time until reduction of layer thickness due to the development of image was remarkably observed.

With the plate developed with each developing solution, the presence of stain or coloration caused by the residual film of the non-image area due to development inferior was confirmed, and the electric conductivity of the developing solution at which the development could be well performed was determined. Further, a limit electric conductivity was determined at which the reduction of layer thickness due to the development was observed to an extent that the reduction of layer thickness was not substantially adversely affect the printing durability of the plate.

A range between the electric conductivity of the developing solution at which the development could be well performed and the limit electric conductivity at which the reduction of layer thickness due to the development was observed to an extent that the reduction of layer thickness was not substantially adversely affect printing

durability of the plate was referred to as the development latitude.

In addition, the similar evaluations were conducted using a developing solution having the composition shown below in place of the DT-2R (1:5 diluted solution).

(Composition of alkali developing solution B)

SiO ₂ .K ₂ O	3.8 parts by weight
(K ₂ O/SiO ₂ =1/1 in molar ratio)	
Citric acid	0.5 parts by weight
Water	95.7 parts by weight

[Evaluation of scratch resistant]

Each of the lithographic printing plate precursors was scratched using a scratching test machine manufactured by HEIDON Co. with applying a load to a sapphire tip (tip diameter: 1.0 mm). Immediately thereafter, the exposed lithographic printing plate precursor was developed using PS Processor LP940H manufactured by Fuji Photo film Co., Ltd., to which a developing solution prepared by diluting Developer DT-2 manufactured by Fuji Photo film Co., Ltd. using 8 parts by volume of water per one part by volume of the developer ("1:8 diluted solution") and a solution prepared by diluting Finisher FG-1 manufactured by Fuji Photo film Co., Ltd. using one part by volume of water per one part by volume of the finisher ("1:1 diluted

solution") had been charged, at a solution temperature of 30°C for a developing time of 12 seconds. Electric conductivity of the developing solution was 43 mS/cm. A numeral value of the load applied, the scratch formed by which was not visually recognized, was determined to evaluate the scratch resistance. It is evaluated that the larger the numerical value, the better the scratch resistance is.

The results of the evaluations are shown in Table 2 below.

TABLE 1

	Support	Copolymer according to invention										Development Latitude		Scratch Resistance
		Amount	Monomer a	Mol %	Monomer b	Mol %	Monomer c	Mol %	Monomer d	Mol %	Molecular Weight	DT-2R	Developing Solution B	
Example 1	D	0.10 g	a-1	18	b-11	82	-	0	-	0	5.5 x 10 ⁵	8 mS/cm	10 mS/cm	15 g
Example 2	E	0.10 g	a-1	22	b-14	78	-	0	-	0	5.5 x 10 ⁵	9 mS/cm	8 mS/cm	20 g
Example 3	B	0.10 g	a-1	24	b-14	76	-	0	-	0	5.5 x 10 ⁵	8 mS/cm	12 mS/cm	20 g
Example 4	F	0.10 g	a-3	30	b-14	70	-	0	-	0	5.5 x 10 ⁵	8 mS/cm	14 mS/cm	25 g
Example 5	F	0.10 g	a-5	15	b-3	85	-	0	-	0	5.0 x 10 ⁵	10 mS/cm	12 mS/cm	20 g
Example 6	B	0.10 g	a-6	24	b-3	76	-	0	-	0	5.0 x 10 ⁵	9 mS/cm	14 mS/cm	15 g
Example 7	D	0.05 g	a-1	14	-	0	c-3	86	-	0	5.0 x 10 ⁵	12 mS/cm	14 mS/cm	25 g
Example 8	F	0.10 g	a-1	25	-	0	c-4	75	-	0	4.8 x 10 ⁵	8 mS/cm	10 mS/cm	20 g
Example 9	B	0.10 g	a-3	28	-	0	c-5	72	-	0	4.8 x 10 ⁵	8 mS/cm	8 mS/cm	20 g
Example 10	F	0.10 g	a-5	30	-	0	c-9	70	-	0	2.9 x 10 ⁵	9 mS/cm	9 mS/cm	18 g
Example 11	F	0.06 g	a-8	35	-	0	c-10	65	-	0	2.9 x 10 ⁵	10 mS/cm	12 mS/cm	20 g
Example 12	F	0.06 g	a-8	15	-	0	c-10	85	-	0	3.5 x 10 ⁵	12 mS/cm	14 mS/cm	25 g
Example 13	F	0.06 g	a-1	8	b-1	40	c-1	52	-	0	3.1 x 10 ⁵	14 mS/cm	8 mS/cm	20 g
Example 14	F	0.06 g	a-1	22	b-1	33	c-1	45	-	0	3.3 x 10 ⁵	8 mS/cm	10 mS/cm	18 g
Example 15	F	0.10 g	a-3	33	b-7	52	c-1	15	-	0	4.0 x 10 ⁵	9 mS/cm	12 mS/cm	20 g
Example 16	F	0.10 g	a-5	5	b-7	43	c-2	52	-	0	5.0 x 10 ⁵	8 mS/cm	11 mS/cm	20 g
Example 17	F	0.10 g	a-6	8	b-4	22	c-2	50	d-1	20	4.8 x 10 ⁵	7 mS/cm	9 mS/cm	15 g
Example 18	F	0.10 g	a-8	26	b-5	9	c-2	30	d-2	35	4.0 x 10 ⁵	10 mS/cm	10 mS/cm	20 g
Example 19	F	0.10 g	a-8	22	b-9	38	c-2	25	d-3	15	3.0 x 10 ⁵	12 mS/cm	8 mS/cm	20 g
Example 20	F	0.10 g	a-12	33	b-10	67	-	0	-	0	4.5 x 10 ⁵	10 mS/cm	9 mS/cm	20 g
Example 21	F	0.10 g	a-12	27	b-10	73	-	0	-	0	5.0 x 10 ⁵	8 mS/cm	10 mS/cm	20 g
Example 22	F	0.10 g	a-14	35	b-14	65	-	0	-	0	4.0 x 10 ⁵	8 mS/cm	12 mS/cm	15 g
Example 23	F	0.10 g	1-17	30	-	0	c-1	70	-	0	3.0 x 10 ⁵	9 mS/cm	10 mS/cm	20 g
Example 24	F	0.20 g	a-18	30	-	0	c-3	70	-	0	3.0 x 10 ⁵	9 mS/cm	10 mS/cm	25 g
Example 25	F	0.30 g	a-20	30	-	0	c-10	70	-	0	3.0 x 10 ⁵	8 mS/cm	10 mS/cm	20 g
Example 26	F	0.40 g	a-21	30	b-10	50	c-1	20	-	0	3.0 x 10 ⁵	10 mS/cm	8 mS/cm	20 g
Example 27	F	0.10 g	a-22	25	b-16	38	c-3	37	-	0	3.0 x 10 ⁵	12 mS/cm	9 mS/cm	18 g
Example 28	F	0.10 g	a-22	22	b-3	26	c-6	52	-	0	3.0 x 10 ⁵	8 mS/cm	11 mS/cm	20 g
Example 29	F	0.10 g	a-24	5	b-3	20	c-10	75	-	0	3.0 x 10 ⁵	8 mS/cm	10 mS/cm	18 g
Example 30	F	0.10 g	a-24	12	b-3	6	c-10	62	d-1	20	3.0 x 10 ⁵	9 mS/cm	11 mS/cm	20 g

Example 31	F	0.10 g	a-30	18	b-3	4	c-6	44	d-2	34	3.0×10^5	9 mS/cm	10 mS/cm	20 g
Example 32	F	0.10 g	a-33	28	b-10	35	c-6	20	d-3	17	3.0×10^5	10 mS/cm	12 mS/cm	15 g
Example 33	F	0.10 g	a-29	30	-	0	-	0	d-3	70	3.0×10^5	12 mS/cm	9 mS/cm	20 g
Example 34	F	0.10 g	a-29	35	-	0	-	0	d-4	65	3.0×10^5	10 mS/cm	8 mS/cm	20 g
Example 35	F	0.10 g	a-34	33	-	0	-	0	d-4	67	3.0×10^5	8 mS/cm	10 mS/cm	20 g
Example 36	F	0.10 g	a-35	30	-	0	-	0	d-5	70	3.0×10^5	9 mS/cm	10 mS/cm	20 g
Example 37	F	0.45 g	a-36	33	-	0	-	0	d-5	67	3.0×10^5	8 mS/cm	12 mS/cm	18 g
Comparative Example 1	F	0.60 g	Methacrylic acid	25	-	0	-	0	d-2	75	5.5×10^5	2 mS/cm	3 mS/cm	2 g
Comparative Example 2	F	0.10 g	Methacrylic acid	20	-	0	-	0	d-2	80	5.8×10^5	2 mS/cm	2 mS/cm	4 g
Comparative Example 3	F	0.10 g	Methacrylic acid	35	-	0	-	0	d-2	65	5.3×10^5	2 mS/cm	2 mS/cm	3 g

Copolymerization monomers used in the copolymer according to the invention shown in Table 1 are described below.

Monomer a: Monomer forming the monomer unit represented by formula (I)

Example compounds a-1 to a-36 described hereinbefore
Monomer b: Styrene derivative

Example compounds b-1 to b-17 described hereinbefore
Monomer c: (Meth)acrylamide derivative

Example compounds c-1 to c-10 described hereinbefore
Monomer d: (Meth)acrylate

d-1: Methyl acrylate

d-2: Methyl methacrylate

d-3: Ethyl methacrylate

d-4: Isopropyl methacrylate

d-5: n-Butyl methacrylate

It can be seen from the results shown in Table 1 that the development latitude is considerably enlarged and the scratch resistance is also dominantly improved with the heat-sensitive lithographic printing plate precursors for Examples 1 to 37 according to the invention in comparison with the heat-sensitive lithographic printing plate precursors for Comparative Examples 1 to 3.

[Advantage of the Invention]

According to the invention, an infrared photosensitive lithographic printing plate precursor, which is capable of being subjected to direct plate-making from digital data of computer or the like and excellent in the scratch resistance and exhibits a broad development latitude, can be provided.

[Name of Document] Abstract

[Abstract]

[Object] To provide an infrared photosensitive lithographic printing plate precursor which is capable of producing a printing plate directly from digital data of a computer or the like and which exhibits a broad development latitude and is excellent in scratch resistance.

[Construction] An infrared photosensitive lithographic printing plate precursor including a support having thereon two layers each containing a polymer insoluble in water and soluble in an aqueous alkaline solution, in which an upper layer of the two layers contains a copolymer including a specific monomer unit.

[Selected Drawing] None